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PROTOCOL TO CHARACTERIZE GASEOUS EMISSIONS AS A
FUNCTION OF FUEL AND ADDITIVE COMPOSITION

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**PROTOCOL TO CHARACTERIZE
GASEOUS EMISSIONS
AS A FUNCTION OF
FUEL AND ADDITIVE COMPOSITION**



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PROTOCOL TO CHARACTERIZE GASEOUS EMISSIONS
AS A FUNCTION OF FUEL-ADDITIVE COMPOSITION

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ABSTRACT

Analytical techniques and equipment were developed and applied to characterize gaseous emissions as a function of fuel/additive composition from two versions of a high production automotive engine. A number of potentially-harmful gaseous emissions were measured at specific mileage intervals on a 1972 and 1975 350 CID Chevrolet engine. Mileage accumulation was accomplished using repetitive 23 minute long driving LA-4 cycles featured in the current Federal light-duty emissions test procedure. The operation of the engine was by means of special stationary dynamometers with an automatic tape-controlled servo-driver. Emission tests were conducted at 0, 1000, and 2000 mile intervals with four fuel/additive packages with each engine using a hot start version of the 1975 light-duty Federal Test Procedure.

In addition to the regulated emissions of unburned hydrocarbons, carbon monoxide, and oxides of nitrogen, a number of additional gaseous and particulate emissions were determined at each emissions inspection on both engines with all four fuel/additive combinations. Sulfur compounds measured included sulfur dioxide, sulfate, hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and ethyl mercaptan. Nitrogen compounds measured were ammonia, dimethylnitrosamine, and nitromethane. In addition, particulate emission rates were determined using a 8 inch dilution tunnel at all engine-fuel combinations at the three emission inspections.

One important aspect of this program was the statistical reliability of the emissions testing. Several types of engine starts (i.e., cold, forced cold, hot) were evaluated, and hot starts were selected for full scale emissions inspection testing. Comparison of emission rate variability of hot starts on engine dynamometers with the standard certification test indicated that hot start dynamometer was a more repeatable test procedure. A limited amount of statistical analysis of the data has also been included. The two engines operating on the short cycle mileage accumulation driving schedule were not found to produce any increase in regulated emissions which could be specifically attributed to the fuel additive packages. The inherent test procedure variability coupled with engine emissions deterioration generally explained any changes in emission rates.

FOREWORD

The work described in this report was performed by Southwest Research Institute for the U.S. Environmental Protection Agency under Contract No. 68-02-1275, "Protocol to Characterize Gaseous Emissions as a Function of Fuel Additive Composition". This research effort was a result of Request for Proposal No. DU-74-B349 and Southwest Research Institute's responding Proposal No. 11-9865, dated November 9, 1973. This project was initiated on February 13, 1974, and the technical effort was completed on April 23, 1975. It was identified within SwRI as Project No. 11-3902.

Project Leader for SwRI was Harry E. Dietzmann, Senior Research Chemist, Department of Emissions Research. Overall supervision has been provided by Karl J. Springer, Director, Department of Emissions Research. Project Officer for the Environmental Protection Agency has been Dr. Ronald L. Bradow, Chief, Emissions Testing and Characterization Section, Chemistry and Physics Laboratory.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
FOREWORD	iv
LIST OF FIGURES	vii
LIST OF TABLES	ix
I. INTRODUCTION	1
A. Approach	1
B. Scope	2
II. TEST PROCEDURES	5
A. Chemical Analysis	5
B. Engine Dynamometer Test Stands	8
C. Test Plan	14
D. Engine Qualification	16
III. RESULTS	21
A. 1972 350 CID Chevrolet Engine	21
B. 1975 350 CID Chevrolet Engine	37
C. Documentation of Engine Deposits	52
D. Statistical Analysis	56
IV. SUMMARY AND CONCLUSIONS	63
LIST OF REFERENCES	67
APPENDIXES	
A. Methods of Chemical Analysis	
B. Individual Hydrocarbon Distribution	
C. Individual Sulfur and Nitrogen Compound Distribution	
D. Sulfur Distribution	

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Several Views of 350 CID Chevrolet Test Stands	9
2	Sulfate Sampling Flow Schematic with Dilution Tunnel Dimensions	13
3	HC Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	26
4	CO Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	27
5	NO _x Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	28
6	SO ₂ Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	29
7	SO ₄ ⁼ Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	30
8	Particulate Emission Rates of 1972 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	31
9	HC Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	41
10	CO Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	42
11	NO _x Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	43
12	SO ₂ Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	44

LIST OF FIGURES (Cont'd)

<u>Figure</u>		<u>Page</u>
13	SO ₄ ⁼ Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	45
14	Particulate Emission Rates of 1975 350 CID Chevrolet Engine at Several Mileage Intervals with the Four Test Fuels	46
15	Typically Cleaned Piston Heads and Cylinder Heads, 1972 Chevrolet 350 Engine	53
16	Typical Piston Deposits from 1972 350 CID Chevrolet Engine Operating on the Four Test Fuels After 2000 Miles of LA-4 Cycles	54
17	Cylinder Head Deposits of 1972 350 CID Chevrolet Engine Operating the Four Test Fuels at 2000 Miles of LA-4 Cycles	55
18	Typically Cleaned Valves and Valve Deposits From 1972 350 CID Chevrolet Engine Operating on Three Test Fuels with 2000 Miles of LA-4 Cycles	57

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Federal Light Duty Emission Standards	14
2	List of Fuel/Additive Combinations	15
3	Mileage Accumulation and Emission Testing Fuel Inspection Data	17
4	1972 and 1975 350 CID Chevrolet Engine Emission Qualification Results	19
5	Qualification Test Emissions Variability	22
6	Summary of Exhaust Emissions of 1972 Chevrolet 350 CID Engine, EM-214-F (Base Fuel at 0.1% S)	23
7	Summary of 1972 350 CID Chevrolet Engine Emission Rates	24
8	Summary of Exhaust Emissions of 1972 Chevrolet 350 CID Engine, EM-215-F (Base Fuel at 0.1% S + 0.378 g/gal Lubrizol 8101)	32
9	Summary of Exhaust Emissions of 1972 Chevrolet 350 CID Engine, EM-216-F (Base Fuel at 0.1% S + 0.486 g/gal Paradyne 506)	34
10	Summary of Exhaust Emissions of 1972 Chevrolet 350 CID Engine, EM-231-F (Base Fuel at 0.1% S + 0.05 g Pb/gal + 0.378 g/gal Lubrizol 8101)	36
11	Summary of Exhaust Emissions of 1975 Chevrolet 350 CID Engine, EM-214-F (Base Fuel at 0.1% S)	39
12	Summary of 1975 350 CID Chevrolet Engine Emission Rates	40
13	Summary of Exhaust Emissions of 1975 Chevrolet 350 CID Engine, EM-215-F (Base Fuel at 0.1% S + 0.378 g/gal Lubrizol 8101)	48

LIST OF TABLES (Cont'd)

<u>Table</u>		<u>Page</u>
14	Summary of Exhaust Emissions of 1975 Chevrolet 350 CID Engine, EM-216-F (Base Fuel at 0.1% S + 0.486 g/gal Paradyne 506)	50
15	Summary of Exhaust Emissions of 1975 Chevrolet 350 CID Engine, EM-218-F (High Aromatic Fuel at 0.1% S + 0.378 g/gal Lubrizol 8101)	51
16	Standard Deviation (S_x) and Standard Deviation in Percent of Mean Value ($\% S_x$) for 1972 350 CID Chevrolet Engine with All Four Test Fuels	58
17	Standard Deviation (S_x) and Standard Deviation in Percent of Mean Value ($\% S_x$) for 1975 350 CID Chevrolet Engine with All Four Test Fuels	59
18	Comparison of Standard Deviation in Percent of Mean Value ($\% S_x$) of Standard Cold Start FTP, Hot Start Qualification Testing and Fuel Scale Hot Start Emission Testing	61

I. INTRODUCTION

The Administrator of the Environmental Protection Agency (EPA) is required by Section 211 of the Clean Air Act^{(1)*} to register all fuels and additives used in interstate commerce. The Administrator is further required that the additive manufacturers document additive effects on gaseous and particulate emissions, control system performance, and visibility. This project was initiated by EPA to develop analytical methods for the sampling and analysis of gasoline exhaust emissions. An additional purpose was to further evaluate the success of a test procedure, selected by EPA and required by the contract, in the detection of effects of fuel additives on the gaseous, particulate, and sulfate emissions from cars. These methods were used to determine if the effects of fuel and additive composition could be observed using the 1975 light-duty (LD) Federal Test Procedure (FTP)⁽²⁾. Research and development efforts were centered on major areas, namely:

development of sampling and measurement procedures for the characterization of automotive exhaust for a wide variety of potentially-harmful exhaust products and

establish the validity of the 1975 LD FTP as a test procedure for determining the effects of fuel/additive combinations on gaseous emissions.

A. Approach

The approach used in this research program resulted from the collective experience of EPA, Southwest Research Institute (SwRI), and others involved in air pollution studies with gasoline additives⁽³⁻⁷⁾. A particular test procedure, called out in the EPA work statement, was to be evaluated with respect to its ability to detect harmful effects of fuel additives on both currently-regulated and non-regulated gaseous emissions. The 1975 Federal light-duty vehicle emissions test procedure was used as the basic method of examining both regulated and non-regulated gaseous exhaust components and sulfuric acid for both catalyst-equipped and non-catalyst engines mounted on engine dynamometer stands. The test facility used Clayton hydraulic dynamometers and fixed inertia flywheels to correct engine dynamometer load simulation problems found in previous EPA programs.

The EPA-selected procedure involved emissions testing by a hot start 31 minute modification of the 1975 Federal Test Procedure after

* Superscript numbers in parentheses designate List of References at the end of this report.

preliminary preconditioning with base fuel, mileage accumulation to 2000 miles using repetitive Federal Urban driving cycles using both additive and base fuels followed by retesting using the modified hot start 1975 FTP.

Final and initial emissions data would be then statistically compared to (a) determine whether or not a significant additive influence was detectable with commercial additive packages and (b) determine on the basis of statistical considerations the magnitude of an effect which would be detectable by this procedure.

Finally, considerations involved in setting up, calibrating, and operating the EPA procedure provided a background of experience in the practicality of the test itself as a fuel additive protocol. A qualitative discussion of the problems incurred at SwRI with this schedule is included in a later portion of this report as a guide for future protocol development work.

The main thrust of this effort was to develop methods to measure both presently regulated and unregulated, potentially harmful gaseous products; however, particulate sampling and sulfate analysis was conducted as well. A variety of analytical methods were used during the course of the study.

Several of the instrumental methods of analysis used in the characterization of automotive exhaust were developed at EPA prior to project initiation. These methods included non-reactive hydrocarbons (NRHC) by gas chromatography and sulfate analysis using the barium chloranilate (BCA) procedure. Measurement of additional compounds for the characterization of emissions was accomplished by SwRI during a procedural phase of the program. Sulfur compounds measured include sulfur dioxide (SO_2), carbonyl sulfide (COS), hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), and ethyl mercaptan ($\text{C}_2\text{H}_5\text{SH}$). Ammonia (NH_3), nitromethane (CH_3NO_2), and dimethylnitrosamine (DMNA) were nitrogen compounds measured to characterize the exhaust as a function of fuel and additive composition. Particulate emission rates were calculated from weight gain on small filters used to collect sulfate using an 8 inch dilution tunnel. Tunnel size selection was based on direct experience of EPA personnel. Regulated emission rates for unburned hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO_x) were obtained using the accepted procedure.

B. Scope

Two versions of a current high production engine were employed in this research effort. The engine selected for this study was a 350 CID Chevrolet engine, a 1975 version complete with EGR, air pump, and GM

oxidation catalyst, and a 1972 version. The fuel was supplied by EPA, and additive selection was made by SwRI with the advice and consent of the EPA Project Officer and included Paradyne 506 and Lubrizol 8101. Engines were mounted on a stationary dynamometer test stand designed to simulate vehicle operation. An automatic tape-controlled servo-driver system was incorporated into the two test stands and was used for mileage accumulation. Characterization emission tests were conducted at specific mileage intervals; namely, 0, 1000, and 2000 miles.

II. TEST PROCEDURES

The characterization of exhaust from the 1972 and 1975 350 CID Chevrolet engines was accomplished using a number of analytical procedures. These methods were available from EPA-RTP or were developed by SwRI during the procedural development phase of the program. Emission tests were conducted at specific intervals on a mileage accumulation schedule. Engine mileage was obtained using an automatic driver on a 24-hour basis using a repetitive driving cycle. The driving cycle specified was the urban dynamometer driving schedule of the 1975 light duty Federal Test Procedure, commonly called the LA-4 driving cycle. Four fuel/additive packages were tested on both engines. Two commercially-available fuel additives were selected for this program and were run using the supplier's suggested fuel treatment concentrations.

A. Chemical Analysis

In addition to the regulated emissions of unburned hydrocarbons, carbon monoxide, and oxides of nitrogen, five additional groups of compounds were measured in the characterization of emissions from the two engines as a function of fuel and additive composition. These groups included a series of non-reactive hydrocarbons, sulfur dioxide, sulfate (SO_4^-), nitrogen compounds and sulfur compounds.

Nitrogen compounds which were determined included ammonia, nitromethane, and dimethylnitrosamine. Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and ethyl mercaptan were sulfur compounds of interest. The following summarizes the compounds measured to characterize emissions along with the methods of detection.

TABLE X. SUMMARY OF ANALYTICAL METHODS

Chemical Analyses	Compounds Detected	Instrument	Detection System
1. non-reactive hydrocarbons (NRHC)	CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , C_6H_6 , C_7H_8	Varian 1740	FID
2. sulfur dioxide	SO_2	TECO Model 40	PF
3. sulfate	SO_4^- (SO_3)	Beckman Model 25	UV
4. nitrogen compounds	ammonia, dimethylnitrosamine, nitromethane	gas chromatograph	ECD
5. sulfur compounds	H_2S , COS, CH_3SH , $\text{C}_2\text{H}_5\text{SH}$	gas chromatograph	FPD

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1. Non-reactive Hydrocarbons (NRHC)

Non-reactive hydrocarbons were measured using a gas chromatograph procedure⁽⁸⁾ developed by EPA. This procedure employs a 4-column arrangement coupled with dual gas sampling valves, pneumatically operated valves programmed electrically. In essence, this procedure allows baseline separation of all C₁ to C₃ hydrocarbons, including air and CH₄. In addition, benzene and toluene are also baseline separated during the same analysis.

Hydrocarbons considered to be non-reactive were methane, ethane, acetylene, propane and benzene. Non-reactive hydrocarbon emission rates were determined by adding the individual NRHC ppmC values for each bag and computing the NRHC emission rates using these values in lieu of the bag cart HC concentrations. The samples were also background corrected, and calculated emission rates were expressed in accord with the usual bag weighting factors.

The NRHC emission rate for a given part of the test was the sum of the individual non-reactive hydrocarbons in ppmC with the appropriate bag weighting factor applied. All bags were analyzed using the procedure specified in the Federal Register⁽²⁾ to obtain HC emission rates. The NRHC/HC is the fraction of non-reactive hydrocarbons in the total hydrocarbons determined by the bag cart, expressed on weighed basis.

In addition to hydrocarbons considered non-reactive (CH₄, C₂H₆, C₂H₂, C₃H₈, and C₆H₆), several other compounds were measured. These compounds included C₂H₄, C₃H₆, and C₇H₈; and consequently, when individual non-reactive hydrocarbon concentrations are presented, these three reactive hydrocarbons are also included. The NRHC samples were obtained from the bag samples obtained during the hot start 1975 LD FTP. Calibration standards were obtained and named using EPA golden standards. Emission rates of reactive and non-reactive hydrocarbons were determined on both engines with all four test fuels. The ratio of NRHC to HC were calculated for all tests where NRHC values were obtained.

2. Sulfur Dioxide (SO₂)

Sulfur dioxide was measured using a TECO Model 40 pulsed fluorescent (PF) SO₂ analyzer. Measurements were obtained using the 1975 LD FTP bag samples as well as continuous on-line monitoring. An integrator was included as an integral part of the CVS to provide the average SO₂ concentrations during these tests.

By obtaining bag and continuous SO₂ values, it was possible to establish the relationship between continuous and bag sampling. Sulfur

balances were calculated on all tests utilizing the SO₂ and sulfate emission rates. In general, the bag SO₂ values were less than the continuous SO₂; and both were in excess of 100 percent sulfur recovery most of the time. A complete description of the measurement of SO₂ using the TECO Model 40 pulsed fluorescent SO₂ analyzer is presented in Appendix A.

3. Sulfate (SO₄⁼)

The measurement of sulfate in the exhaust was measured using the barium chloranilate procedure. This method involves collecting under quasi-isokinetic conditions, a sample of exhaust sulfate on a 47mm 0.5 micron fluoropore (FH) filter, extraction with 60 percent isopropyl alcohol (IPA) and analysis using a recording UV colorimeter at 310nm. Sulfuric acid standards were used to calibrate the system and determine sulfate filter concentrations.

Prior to obtaining a sulfate sample, each filter was weighed on a microgram balance under a controlled environment and then again after each sample was obtained and before the extraction step. The controlled environment for the microgram balance was maintained at 72° ± 1°F (dry) and 57° ± 1°F (wet), providing an absolute humidity of 46 ± 2 grains H₂O per pound dry air and a relative humidity of 39 percent. By obtaining the particulate weight, it was possible to determine what fraction was sulfate of the total particulate as well as the particulate emission rates.

Both sulfate and particulate weights were obtained using a single filter for the entire 31 minute 1975 LD FTP. The 31 minute duration consisted of the hot start 23 minute LA-4 driving cycle plus the first 505 seconds of the next LA-4 test following a 10 minute soak. The sulfate and particulate emission rates are not weighted in accordance with the 1975 FTP, since only one sample was obtained and, therefore, must be viewed accordingly. The SO₄⁼ and particulate weights were simply divided by the kilometers driven to obtain g/km for the engines, fuels, and additives tested.

The barium chloranilate detection method was used throughout the program for sulfate collected samples and proved to be a precise, reliable analytical tool. A number of standards were exchanged between EPA (Ann Arbor), EPA (RTP), and SwRI; and the correlation between laboratories was satisfactory. A thorough description of the sampling system interface, dilution tunnel, and the analytical instrumentation is presented in Appendix A.

4. Nitrogen Compounds

Nitrogen compounds measured included ammonia, dimethylnitrosamine, and nitromethane. Samples were analyzed from the 1975 LD FTP

bags, and the concentration of individual compounds was determined. Individual standards were prepared for the quantitative determination of each of the nitrogen compounds. The NH_3 , CH_3NO_2 , and DMNA were measured using a gas chromatograph system equipped with an electrocoulometric detector (ECD). Of all three compounds, only CH_3NO_2 was observed in the majority of bag samples. This procedure is described more thoroughly in Appendix A.

B. Engine Dynamometer Test Stands

Two engine dynamometer stands were constructed using water brake absorbers removed from Clayton CT-200 chassis dynamometers. The shaft used to connect the automatic transmission output and the absorber also held an inertia wheel and a hydraulic disc brake. The rpm signal obtained from the tach generator of the Clayton unit was calibrated in miles per hour, permitting a standard driving aid to be used as a speed readout; and the entire torque arm-load cell-readout system from the Clayton was retained intact for setting road loads. Several views of the engine dynamometer stands and control systems are shown in Figure 1.

One major advantage of this system is that the power absorption curve is intrinsically similar to that of the water-brake chassis dynamometer systems commonly used for LA-4 vehicle tests. The proper simulation of road load (as it varies with speed) by electric dynamometers is a complex and expensive process, and often the accuracy of the simulation is not as good as expected. Once calibrated, the water brake system essentially reproduces the chassis dynamometer results faithfully. In addition, since the water absorber "loads up" by itself as speed increases, no control loop is required for that purpose; and engine control becomes simply a matter of throttle or brake application as required to follow the LA-4 trace.

The system controls simulate those in an automobile, permitting throttle and brake application by an operator for system checkouts, procedural development, or in the event of equipment failure to prevent excessive downtime during repairs. For mileage accumulation, an automatic control loop utilizing the HYTRESS (Highway Test Recorder and Simulator System), manufactured by Dynamic Precision Controls Corporation, was used. This unit was mounted under the operator's seat and could be readily disconnected when not in use. With the exception of a slight delay and then a slight overshoot on rapid accelerations and decelerations, the driving trace using the automatic control system was essentially identical to driving traces obtained during manual driving.

The ratio of tire diameter to Clayton dynamometer roller diameter has been determined to be 3.07 for the standard 1972 and 1973 Chevrolet Bel Air and Impala automobiles. Therefore, the rotational speed of the

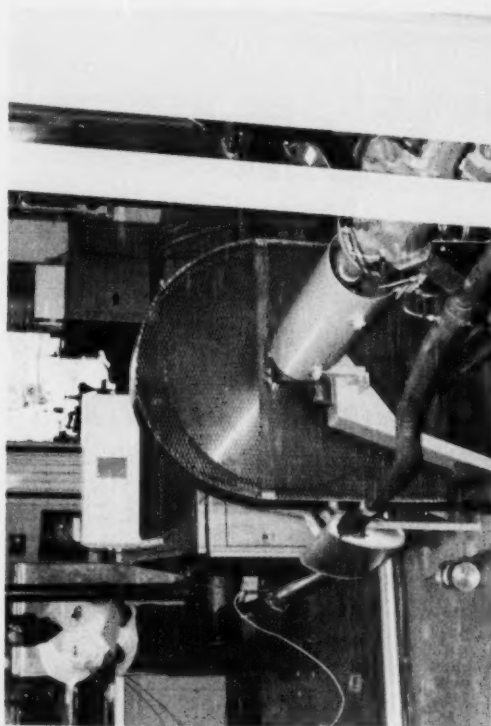
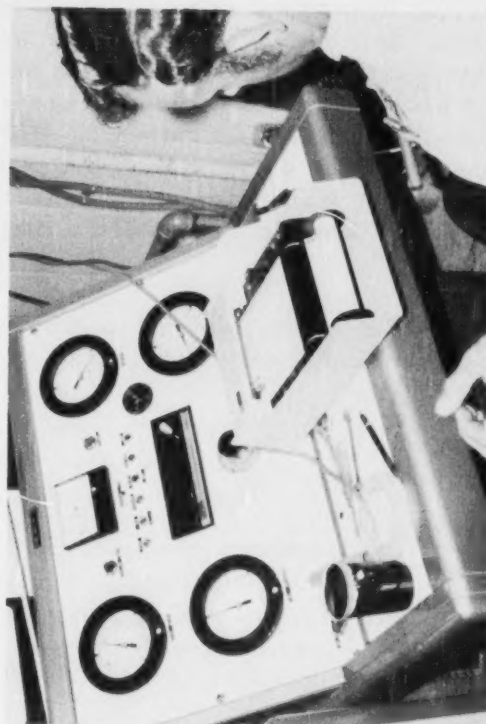
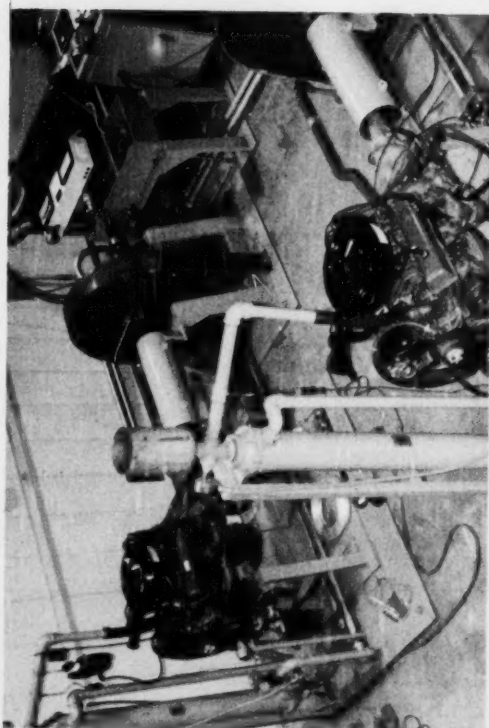
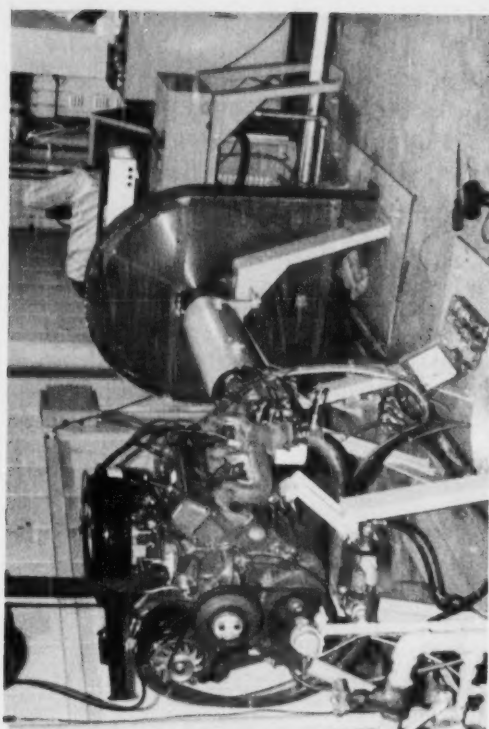


FIGURE 1. SEVERAL VIEWS OF 350 CID CHEVROLET TEST STANDS

Clayton dynamometer would equal the rotational speed of the transmission output shaft if the rear axle ratio was 3.07. The Chevrolet Bel Air and Impala standard rear axle ratios were 3.08 in 1972 and 2.73 in 1973. For this project, it was decided to use a single axle ratio for both of the two engines; and the 3.08 ratio was selected. Therefore, in the test stands constructed, the dynamometer to transmission output speed relationship for the test stand versus the vehicle with standard axle ratio was identical for the 1972 model and varied a little more than 10 percent for the 1973 model.

The inertia wheel was a solid mild steel disc with an OD/ID 75. The general formulas used to determine the inertia wheel dimensions are:

$$D(\max) = \frac{30,000}{N(\max)} \quad I_w = 0.0003986TD^4 \quad W_w \approx 0.006145TD^2$$

D = diameter of inertia wheel, cm

N = speed, rad/sec

T = thickness of inertia wheel, cm

I_w = inertia of wheel, kg - m²

W_w = weight of wheel, kg (disregarding center hole)

In the dynamometer test stands, the dynamometer speed is equal to the transmission output speed. Therefore, the following equations were derived and used to establish the relationship between the test stand dynamometer speed and the chassis dynamometer speed.

$$\frac{\text{stationary test stand dynamometer speed}}{\text{chassis dynamometer speed}} = 21.91 \left(\frac{\text{axle ratio}}{\text{effective tire diameter}} \right)$$

$$I_w = 0.000025 W_v \left(\frac{\text{effective tire diameter}}{\text{axle ratio}} \right)$$

Effective Tire Diameter in Centimeters

Several methods were evaluated for determining the proper dynamometer horsepower to be set on the test stand dynamometer. The test stand does not have a differential, rear axle bearings, tire to dynamometer roll friction, etc.; and therefore, these must be accounted for in the horsepower set into the dynamometer. For determination of the horsepower setting, a 1972 Chevrolet Impala with a 350 CID engine and automatic transmission was used. This automobile and the test stands were essentially identical with respect to the engine and the automatic transmission.

The simulation of the automobile on a test stand can be accomplished by simulating the total inertia and horsepower from the transmission

onward through the drive system and the dynamometer. This horsepower was determined with the transmission in neutral using the method in Appendix II of the Federal Register for the Control of Air Pollution - New Motor Vehicles and New Motor Vehicle Engines. Initially, the road load horsepower and inertia prescribed in the Federal Register (12.7 and 4500 respectively) were set into the chassis dynamometer. Coast down times were determined on the 1972 Chevrolet and also on an available 1973 Ford. The times were essentially the same for both vehicles indicating that the horsepower absorbed in the drive systems was essentially the same. The total horsepower was calculated from the coast down times using the method in the Federal Register. This test was conducted with the transmission in neutral with a 12.7 hp road load and 4500 lb inertia. This calculated horsepower value was then used for setting up the horsepower on the test stand, and coast downs were determined on the test stand. The coast down times obtained on the test stands were essentially the same as those obtained with the vehicle on the chassis dynamometer. These and other data are summarized below:

Horsepower Calculated From 55 to 45 mph Coast Downs			
Vehicle	Operation	Coast Down Time, sec	Calculated hp
1972 Chevrolet Impala	dyno	15	18
1972 Chevrolet Impala	dyno	16	17
1972 Chevrolet Impala	road	16	--
1973 Ford LTD	dyno	15	18

Test Stand	Total Load, hp	Coast Down Time, sec.
Engine No. 1	18	15
Engine No. 2	18	15

Other determinations included: the coast down times for the vehicles on level roadway, the vacuum at constant 50 mph on level roadway and on the chassis dynamometer, and the fuel consumption rate with the vehicle held at 50 mph on the chassis dynamometer. These results are summarized below:

Data at 50 mph Constant Speed			
	Set Road Load, hp	Manifold Vacuum, " Hg	Fuel Rate, lb/min
Vehicle on Dynamometer	12.7	18.5	0.24
Vehicle on Road	----	18.1	----
Engine No. 1	12.7	17.9	0.25
Engine No. 2	12.7	18.1	0.24

In addition, engine backing at cut-throttle was determined to be approximately 15 hp at 50 mph using the coast down procedure. All of these evaluations indicated that the horsepower set into the test stand dynamometer was reasonably indicative of road-load horsepower at an equivalent speed.

It is recognized that friction horsepower essentially increases linearly with speed and aerodynamics; horsepower increases essentially as the cube of the speed. Therefore, the resultant horsepower as the speed decreases is dependent on the ratio of the friction to aerodynamic horsepower. Just as some difference occurs between horsepower on the road and the chassis dynamometer over a wide speed range, some difference will occur between these test stands, the chassis dynamometer, and the road. In a cycle such as the LA-4, however, where fairly rapid accelerations and decelerations are the dominant feature, inertia (not road-load horsepower) is the dominant factor affecting emissions. At slower vehicle speeds, the road-load horsepower is a relatively small portion of the total horsepower generated during a rapid acceleration; and rapid decelerations are controlled by braking, with road-load horsepower being of essentially no significance. At higher speeds, where road-load horsepower is more significant, all systems have been calibrated to essentially the same equivalent horsepower. Therefore, both the chassis dynamometer and these test stands adequately simulate road operation for cyclic tests such as the LA-4.

Mileage accumulation was obtained using an automatic driver system on both engine stands. Repetitive LA-4 cycles were used as the mileage accumulation cycle throughout the program. The automatic drivers were used on a 24-hour basis to obtain the mileage in as short a time as possible. Emission tests were conducted using a manual driver and hot start LA-4 tests of 31 minute duration. A 2.54 m (10 foot) long by 21.3 cm (8.4 inch) ID stainless steel dilution tunnel was used to obtain "isokinetic" fluoropore filter samples for sulfate and particulate analysis. This system was designed basically for the analysis of sulfate, since the SO_3 initially formed acts as both a gas and a particle. The construction of the tunnel was for $\text{SO}_4^{=}$ measurements. However, it was possible to weigh the filters before and after each test to obtain an indication of particulate emission rates. A flow schematic of the "mini tunnel" along with the critical dimensions is presented in Figure 2. This research effort was not intended to be a particulate study, and no correlation with the EPA standard 45.7 cm (18 inch) dilution tunnel was performed.

The contractual requirement to report all data and results in modernized metric units (SI) requires a statement of equivalent emission standards for 1973 and later model year light-duty cars in grams per kilometers (g/km) for understanding. Table 1 lists the HC, CO, and NO_x limits in g/km with those published in appropriate Federal Registers in

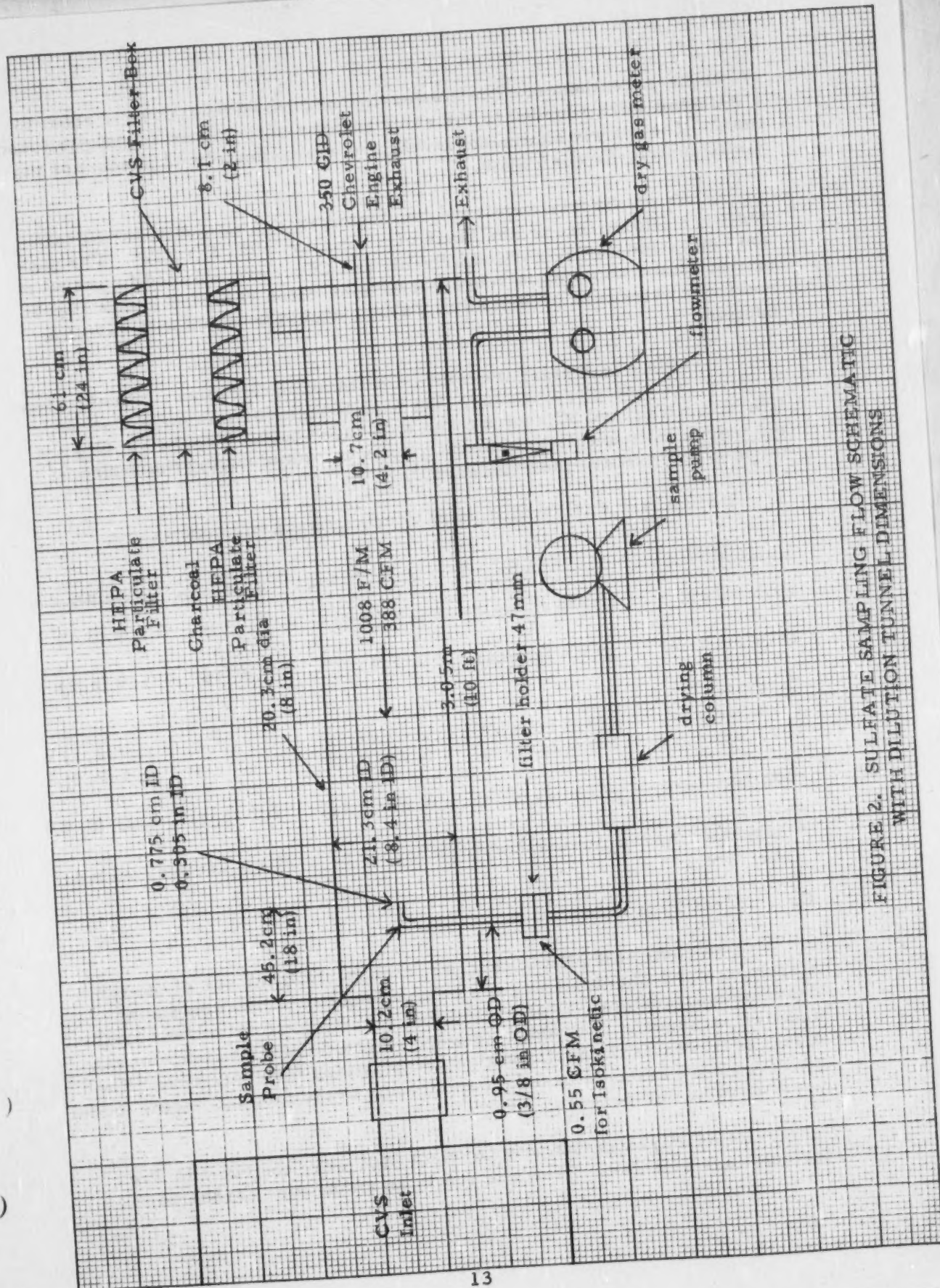


FIGURE 2. SULFATE SAMPLING FLOW SCHEMATIC
 WITH DILUTION TUNNEL DIMENSIONS

g/mile in parentheses. The conversion was based on 1.609 km equal to 1 mile and were rounded to the same number of decimals as the published limit. The metric equivalent levels are approximately 62 percent of the mixed metric-English units.

As previously mentioned, emission rates calculated during this research effort were on the basis of a hot start 1975 LD FTP. The gaseous emission rates, particularly HC and CO, were affected by hot start testing; and comparisons between emission rates reported in this report and those standards presented in Table 1 should be made with extreme caution.

Table 1 is merely included as a frame of reference. Please keep in mind, as mentioned earlier, that even though gaseous emissions of HC, CO, NO_x, and SO₂ were taken on a three bag 1975 LD FTP (from a hot start), only one sample for SO₄⁻ was collected during the entire 31 minutes (23 minutes plus 505 seconds).

TABLE 1. FEDERAL LIGHT DUTY EMISSION STANDARDS

Year	Units	HC	CO	NO _x
1973 - 1974	g/km (g/mile)	2.1 (3.4)	24 (39)	1.9 (3.0)
1975 Interim	g/km (g/mile)	0.9 (1.5)	9.3 (15)	1.9 (3.1)
Original				
1975 Statutory	g/km (g/mile)	0.25 (0.41)	2.1 (3.4)	1.9 (3.1)
1977 Statutory*	g/km (g/mile)	0.25 (0.41)	2.1 (3.4)	1.3 (2.0)
1978 Statutory*	g/km (g/mile)	0.25 (0.41)	2.1 (3.4)	0.25 (0.40)

* suggested by the Administrator on March 6, 1975 but not yet enacted into law

C. Test Plan

The basic test plan of this program involved the use of the two aforementioned Chevrolet engines on a mileage accumulation engine dynamometer system. Each engine was run using a total of four fuel/additive packages. Two additives were selected from a number of candidate additives as the fuel/additive combinations for evaluation. The additives were selected based on application to the fuel and engine model years used in this research effort.

Enjay Paradyne 506 and Lubrizol 8101 were the two additive formulations selected. Paradyne 506 is an amine type carburetor

detergent with multifunctional additives to reduce rust, engine sludge, and water miscibility. The Lubrizol 8101 additive is also a nitrogen containing additive typically employed as a carburetor detergent. Anti-rust and anti-icing additives are also included in the Lubrizol 8101 additive package. Enjay Paradyne 506 was added to the fuel in the manufacturer's recommended treatment level of 45 PTB (0.486 g/gal). The supplier's recommended treatment level for Lubrizol 8101 was 35 PTB (0.378 g/gal). A list of the fuel/additive combinations used for each of the engines is presented in Table 2.

TABLE 2. LIST OF FUEL/ADDITIVE COMBINATIONS

<u>Engine Description</u>	<u>Fuel Code</u>	<u>Fuel Additive Description</u>
1972 350 CID Chevy	EM-214-F	Base fuel at 0.1% S
1972 350 CID Chevy	EM-215-F	Base fuel at 0.1% S + 0.378 g/gal Lubrizol 8101
1972 350 CID Chevy	EM-216-F	Base fuel at 0.1% S + 0.486 g/gal Paradyne 506
1972 350 CID Chevy	EM-231-F	Base fuel at 0.1% S + 0.378 g/gal Lubrizol 8101 + 0.05 g/gal Pb
1975 350 CID Chevy	EM-214-F	Base fuel at 0.1% S
1975 350 CID Chevy	EM-215-F	Base fuel at 0.1% S + 0.378 g/gal Lubrizol 8101
1975 350 CID Chevy	EM-216-F	Base fuel at 0.1% S + 0.486 g/gal Paradyne 506
1975 350 CID Chevy	EM-218-F	High aromatic fuel at 0.1% S + 0.378 g/gal Lubrizol 8101

The first three additive combinations were identical for both engines. These included base fuel, base fuel with Lubrizol 8101, and base fuel with Paradyne 506. The fourth fuel/additive combination utilized Lubrizol 8101 at 0.1 percent sulfur level but with two different base fuels. Tests with the 1975 350 CID engine were conducted using a high aromatic fuel with the Lubrizol 8101 at a 0.1 percent sulfur level. Tests with the 1972 350 CID Chevrolet engine were conducted using the original base fuel with Lubrizol 8101 at 0.1 percent S but with 0.05 g/gal Pb added.

The base fuel was supplied by EPA and was used for both mileage accumulation and emission testing. The high aromatic fuel was obtained

from the American Oil Company and the fuel inspection data for both fuels is presented in Table 3. The fuels were supplied in 55-gal drums and each drum was blended individually. Both fuels were doped with thiophene to obtain the desired 0.1 percent sulfur level. Emission tests for a given fuel/additive combination were conducted on fuel from a given drum at the three mileage accumulation test intervals.

During the procedural development phase of the program, the catalyst had sufficient hours of repetitive LA-4 operation to insure catalyst break-in. Once the emission testing was initiated for record, it was felt that the catalyst had in excess of 600 miles of LA-4 operation. Prior to testing a given fuel/additive combination the cylinder heads were removed and cleaned. Valves were cleaned and lapped. The exhaust system was cleaned or replaced, the only portion remaining unchanged was the catalyst in the 1975 350 CID Chevrolet engine.

A minor tune-up was also performed, which included points, plugs, condenser prior to testing each fuel/additive combination. After re-assembling the engine and performing the necessary tune-up steps, the engine went through a short conditioning period to burn-out any residual oils in the new exhaust system and to allow seating of engine components.

Due to the nature of the objectives of this program, it was decided to use a hot start 1975 LD FTP as the test procedure in this study. Each test that is reported in this report is based on a hot start LA-4. Each test was preceded by a 23-minute LA-4 and then a 10-minute soak. After the 10-minute soak, the engine was started and the three bag 1975 LD FTP was run from that point. The first two bags were obtained during the first 23 minutes and the third bag obtained during the first 505 seconds for the second 23 minute run. Although the mileage accumulation was obtained using an automatic driver, the emission tests were performed using a manual driver.

The emission test intervals were at 0, 1000 and 2000 miles. In most cases, three 1975 LD FTP tests were conducted on both engines with each fuel/additive combination. When emissions data was repeatable only two tests were conducted. As part of the characterization portion of the program, measurement of NRHC, sulfur and nitrogen compounds were conducted only on the first two runs.

Generally, if a given test was repeated, SO_2 , $\text{SO}_4^{=}$ and particulate were also obtained. After the final test for a given fuel/additive combination at 2000 miles, then the engine was disassembled, cleaned and readied for the next fuel/additive package.

D. Engine Qualification

Engine qualification tests were conducted on both engines during the initial phase of the program. Emission specifications were pre-

TABLE 3. MILEAGE ACCUMULATION AND EMISSION TESTING
FUEL INSPECTION DATA

<u>Analysis</u>	<u>Base Fuel (EM-214-F)</u>	<u>High Aromatic Fuel (EM-217-F)</u>
Distillation, ASTM D-86, °F		
10%	123	125
50%	199	205
90%	325	340
EP	383	390
Gum, ASTD D-381, mg	4.8	5.2
Sulfur, ppm	190	40
Stability, D-525, hrs	24+	24+
Phosphorous, ppm	1	-
Research Octane Number	93.2	-
Motor Octane Number	84.7	-
Lead, g/gal	nil	nil
FIA Analysis, D-1319		
Aromatics, %	24.0	52.0
Olefins, %	8.3	4.3
Paraffins, %	67.7	43.7

sented by EPA for the engines to be accepted for mileage accumulation. Since the type of start was not specified, a number of emission tests were conducted using three different types of starts on both test stands. They were cold starts, force-cooled starts and hot starts.

The force cooled starts were conducted using a given set of pre-determined conditions to insure repeatable test conditions. After the initial cold start had been completed, the engine was shut off and cooling water was forced through the engine. A fan was used to force lab air over the engine and once the engine had been cooled down and remained stable at not more than 3°F above ambient temperature, the engine was ready for 1975 LD FTP testing. Similar force cooling procedures have been used quite satisfactory in other projects.

An alternative procedure for conducting the mileage accumulation emission testing was to use a hot start rather than force cooled or cold starts. A procedure was readily devised for obtaining repeatable hot start emission data. One advantage of using hot starts was to enable the tunnel to be pre-heated to a consistent temperature. This aided in the preservation of sample integrity, especially for the reactive sulfur containing compounds during the start-up and initial warm-up period of the tunnel prior to the CVS. It was uncertain as to the fate of SO₂ and SO₃ if the tunnel wall temperature changes significantly during the first 505 seconds of the 1975 LD FTP. This uncertainty was eliminated by employing hot starts exclusively during the mileage accumulation emission testing. Further, sulfate testing required an initially preheated engine exhaust system to avoid losses from condensing water, which normally occurs in cold start testing.

The EPA emission specifications, along with the emission results for both test stands for the three types of starts are presented in Table 4. Investigation of the effect of type of start on emission rates provided data which proved to be useful in the selection of type of start. When summarizing the emission results, it became apparent that the hot start produced somewhat more consistent results. The data in Table 4 illustrate that the engines do and do not fall within the contract specifications, depending on the type of start used in conducting the tests.

Since the emission rates were definitely influenced by type of engine start, and more consistent results were obtained using hot starts, all emission testing during the mileage accumulation phase was conducted using hot starts. This decision was in concurrence with the Project Officer and engines were deemed acceptable for fuel/additive testing.

TABLE 4. 1972 AND 1975 350 CID CHEVROLET ENGINE
EMISSION QUALIFICATION RESULTS

1975 LD FTP Emission Rates		EPA Specifications*		SwRI Emission Results			
		Max	Min	Run	Cold	Force Cold	Hot Start
HC, g/km	1972	2.5	1.5	1	2.06	1.82	1.56
				2	2.05	1.79	1.43
				3	-	2.00	1.45
				Avg.	2.06	1.87	1.48
HC, g/km	1975	0.3	0.2	1	0.34	0.23	0.13
				2	0.46	0.18	0.14
				3	0.28	0.21	0.14
				4	0.39	0.27	0.14
				Avg.	0.37	0.22	0.14
CO, g/km	1972	22	12	1	28.16	21.99	20.13
				2	26.43	23.54	18.34
				3	-	21.84	20.99
				Avg.	27.30	22.46	19.82
CO, g/km	1975	2.1	1.7	1	4.09	2.71	1.16
				2	4.98	2.70	1.13
				3	4.09	2.56	1.61
				4	4.70	2.99	1.87
				Avg.	4.47	2.74	1.44
NO _x , g/km	1972	2.5	1.9	1	1.74	1.58	1.70
				2	1.60	1.71	1.73
				3	-	1.84	1.61
				Avg.	1.67	1.71	1.68
NO _x , g/km	1975	1.9	1.6	1	1.14	1.24	1.16
				2	1.26	1.12	1.19
				3	1.17	1.08	1.12
				4	1.26	1.24	1.12
				Avg.	1.21	1.17	1.15

*EPA Specifications did not state type of start

III. RESULTS

The nature of the test matrix for the characterization of emissions as a function of fuel/additive combinations necessitates comparisons between these test fuels on each engine separately. Comparisons of emission rates between engines for a given fuel/additive package are not presented; although, data is included if comparisons are desired.

The question of test repeatability is significant in the potential conclusions from this research effort. For example, historic values of standard deviations in FTP testing in percent of mean value are 13.0 percent for HC, 18.2 percent for CO, and 9.1 percent for NO_x . In the cold, forced cold, and hot start qualification tests, emission variability is presented in Table 5. Based on results of these experiments, it was felt that hot starts would give the best overall test repeatability.

One of the primary objectives of this program was to establish whether the 1975 LD FTP would be sufficiently sensitive to detect changes in emissions as a function of fuel/additive packages. With this in mind, a number of curves were determined for six different emissions to establish the fuel/additive packages as a function of LA-4 mileage accumulation.

These curves must be viewed in the proper perspective with regard to emission test variability when looking for fuel additive effects. In a number of cases, emission trends were observed but careful analysis of test variability indicated that these trends were actually within the test variability itself.

A. 1972 350 CID Chevrolet Engine

For the purposes of this report, the results from the 1972 engine will be discussed first. This engine was used in evaluation of the four fuel/additive packages. These test fuels were coded EM-214-F, EM-215-F, EM-216-F and EM-231-F.

1. EM-214-F Base Fuel at 0.1 Percent Sulfur

The first fuel tested was the base fuel at 0.1 percent sulfur (EM-214-F) and the results of each individual test are shown in Table 6. A summary of these test results is presented in Table 7. The HC emission rates were essentially constant over the 2000 mileage accumulation schedule. The CO emission rates increased slightly, from 18.16 to 21.14 g/km, although within the test variability. The NO_x emission rates decreased from 2.04 to 1.59 g/km over the additional miles. The SO_2 (bag) emission rates decreased from 0.30 to 0.23 g/km, and the SO_2 (continuous) decreased from 0.41 to 0.34 g/km. The sulfate emission

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TABLE 5. QUALIFICATION TEST EMISSIONS VARIABILITY

Emission	Cold Start				Forced Cold				Hot Start			
	72		75		72		75		72		75	
	σ	%	σ	%	σ	%	σ	%	σ	%	σ	%
HC	0.01	0.3	0.08	20.8	0.11	6.0	0.04	16.9	0.07	4.7	0.01	3.6
CO	1.22	3.2	0.45	5.0	0.94	4.2	0.18	6.6	1.35	6.8	0.34	25.0
NO _x	0.10	5.9	0.06	5.1	0.13	7.6	0.11	7.0	0.06	3.7	0.03	2.9

TABLE 6. SUMMARY OF EXHAUST EMISSIONS OF 1972 CHEVROLET 350 CID ENGINE
EM-214-F (BASE FUEL at 0.1% S)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC(1) HC	SO ₂ (b)(2) SO ₂ (c)	SO ₄ = (3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**			
0 miles	12/16/74	1	1.74	0.25	18.87	2.02	0.28	0.42	0.0004	0.67	0.04
		2	1.44	0.22	17.45	2.06	0.31	0.40	0.0004	0.78	0.08
		Avg.	1.59	0.24	18.16	2.04	0.30	0.41	0.0004	0.73	0.06
1000 miles	12/23/74	1	1.56	0.25	20.13	1.70	0.26	0.35	0.0002	0.74	0.02
		2	1.43	0.20	18.34	1.73	0.28	0.32	0.0003	0.88	0.03
		Avg.	1.50	0.23	19.23	1.72	0.27	0.34	0.0003	0.81	0.03
2000 miles	12/31/74	1	1.45	0.31	20.99	1.61	0.23	0.35	0.0004	0.66	0.03
		2	1.41	0.30	21.29	1.56	0.23	0.33	0.0003	0.70	0.04
		Avg.	1.43	0.31	21.14	1.59	0.23	0.34	0.0004	0.68	0.04

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄ = /particulate indicates the fraction of SO₄ = in the particulate

TABLE 7. SUMMARY OF 1972 350 CID CHEVROLET ENGINE EMISSION RATES

Exhaust Species	1975 LD FTP (Hot Start) Emission Rate, g/km											
	EM-214-F			EM-215-F			EM-216-F			EM-231-F		
	0	1000	2000	0	1000	2000	0	1000	2000	0	1000	2000
HC	1.59	1.50	1.43	0.99	0.75	0.77	1.35	0.96	0.83	1.02	0.89	0.88
NRHC	0.24	0.23	0.31	0.15	0.12	0.14	0.25	0.12	0.15	0.19	0.16	0.18
NRHC/HC	0.15	0.15	0.21	0.15	0.16	0.18	0.18	0.12	0.18	0.19	0.18	0.19
CO	18.16	19.23	21.14	12.96	11.60	13.14	23.62	11.85	13.30	18.40	16.63	16.36
NO _x	2.04	1.72	1.59	1.39	1.56	1.51	1.81	1.48	1.60	1.32	1.55	1.38
SO ₂ (b)	0.30	0.27	0.23	0.30	0.30	0.30	0.31	0.27	0.29	0.25	0.33	0.22
SO ₂ (c)	0.41	0.34	0.34	0.39	0.37	0.37	0.40	0.34	0.33	0.39	0.41	0.36
SO ₂ (b)/SO ₂ (c)	0.73	0.81	0.68	0.77	0.81	0.81	0.78	0.81	0.88	0.64	0.80	0.61
SO ₄ **	0.4	0.3	0.4	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.4
Part. *	7.2	11.6	9.9	3.5	4.1	5.3	5.1	6.6	5.2	3.3	6.2	5.1
SO ₄ =/Part.	0.06	0.03	0.04	0.11	0.08	0.06	0.01	0.03	0.04	0.05	0.03	0.08

* mg/km

rates remained relatively constant at 0.4 mg/km, while the particulate emission rates ranged between 7.2 to 11.6 mg/km.

The effect of mileage accumulation on HC, CO and NO_x emission rates is presented in Figures 3, 4, and 5 respectively. Figures 6, 7, and 8 illustrate the effect of mileage accumulation on the emission rates of SO₂, SO₄⁼ and particulate respectively.

The ratio of NRHC/HC ranged from 0.15 to 0.21; whereas the SO₂ (b)/SO₂ (c) ratio ranged from 0.68 to 0.81 and the SO₄⁼/particulate varied from 0.03 to 0.06. The sulfur recoveries based on bag SO₂ values ranged from 60-96 percent while the continuous SO₂ sulfur recoveries ranged from 110-135 percent. The bag SO₂ emission rates averaged about 0.74 of the continuous SO₂ concentrations. Of the fuel sulfur, less than 0.1 percent appears as sulfate, and of the particulate the sulfate was about 4 percent of the total weight.

Characterization of the exhaust of the 1972 350 CID Chevrolet engine operating on EM-214-F for sulfur and nitrogen compounds is presented in Table C-1 of Appendix C. Of all of the compounds to be determined, only one was found on a routine basis. Only trace quantities of COS and H₂S were detected upon occasion and under no tests was CH₃SH and C₂H₅SH detected. The analysis for ammonia and dimethylnitrosamine indicated that neither of these compounds were present in any of the bag samples at any of the mileage test intervals. Of all the nitrogen and sulfur compounds included in the analysis, only nitromethane was detected on a regular basis. First and third bag values were typically 0.15-0.20 ppm and the second bag ranged from 0.05-0.12 ppm. Individual non-reactive and several reactive hydrocarbons were measured during each test and the raw data is presented in Table B-1 of Appendix B.

2. EM-215-F Base Fuel, 0.1 Percent Sulfur with 0.378 g/gal Lubrizol 8101

This fuel/additive package involved the use of the base fuel doped with thiophene to achieve a 0.1 percent sulfur level. In addition, 0.378 g/gal of Lubrizol 8101 was added. The emission rates of all tests conducted on the 1972 350 CID Chevrolet engine with EM-215-F is presented in Table 8. A summary of all the emission rates is included in Table 7 for comparison to other fuel/additive packages.

The HC emission rates decreased from 0.99 to about 0.76 g/km from the 0-mile to the 1000-and 2000-mile emissions inspection. Figure 3 (hexagon shaped points) illustrates the effect of mileage accumulation on the HC emission rates using EM-215-F in the 1972 engine. The CO emission rates ranged from 11.60 to 13.14 g/km and can be seen as a function of mileage accumulation in Figure 4. Only a slight increase in NO_x emission

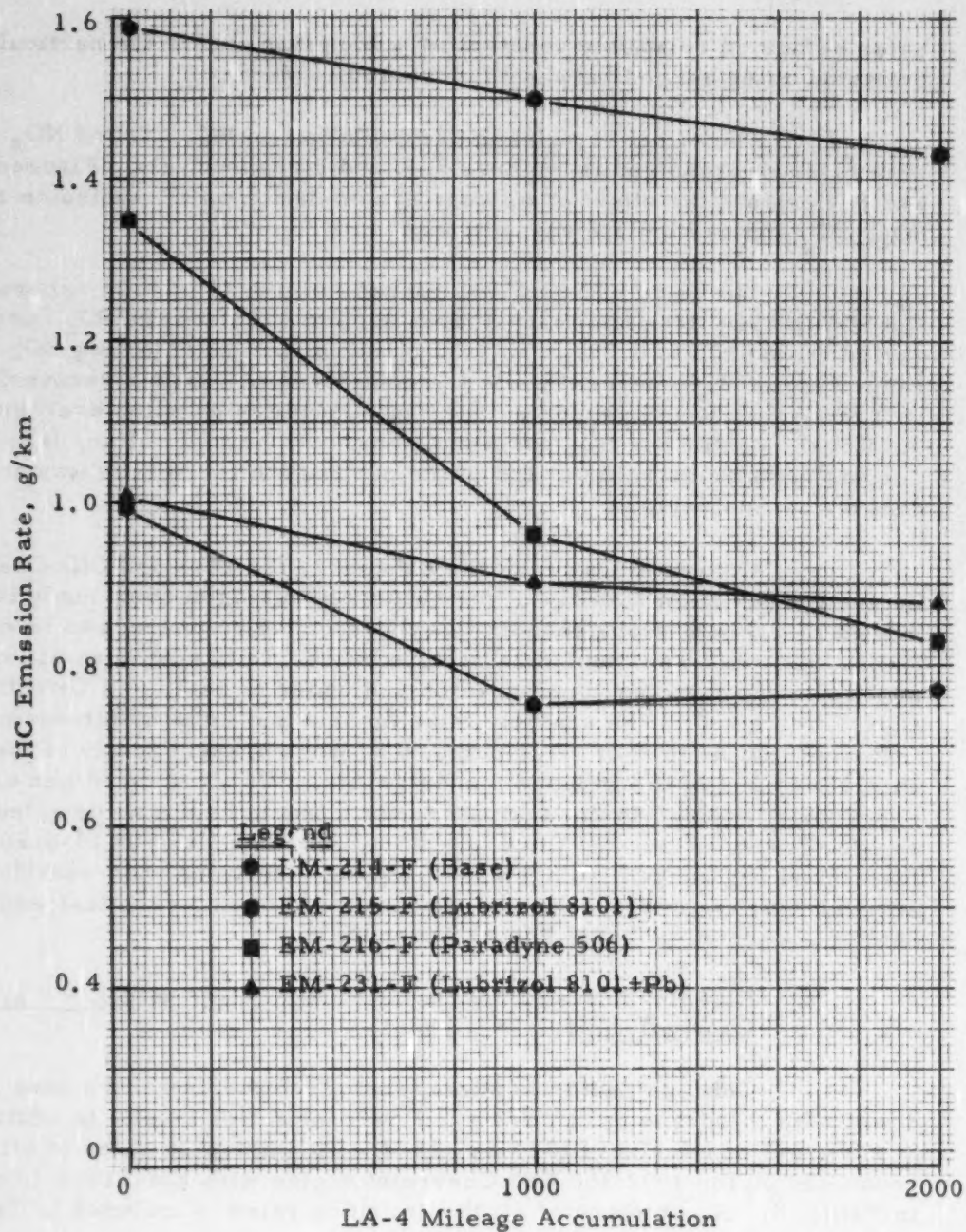


FIGURE 3 . HC EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

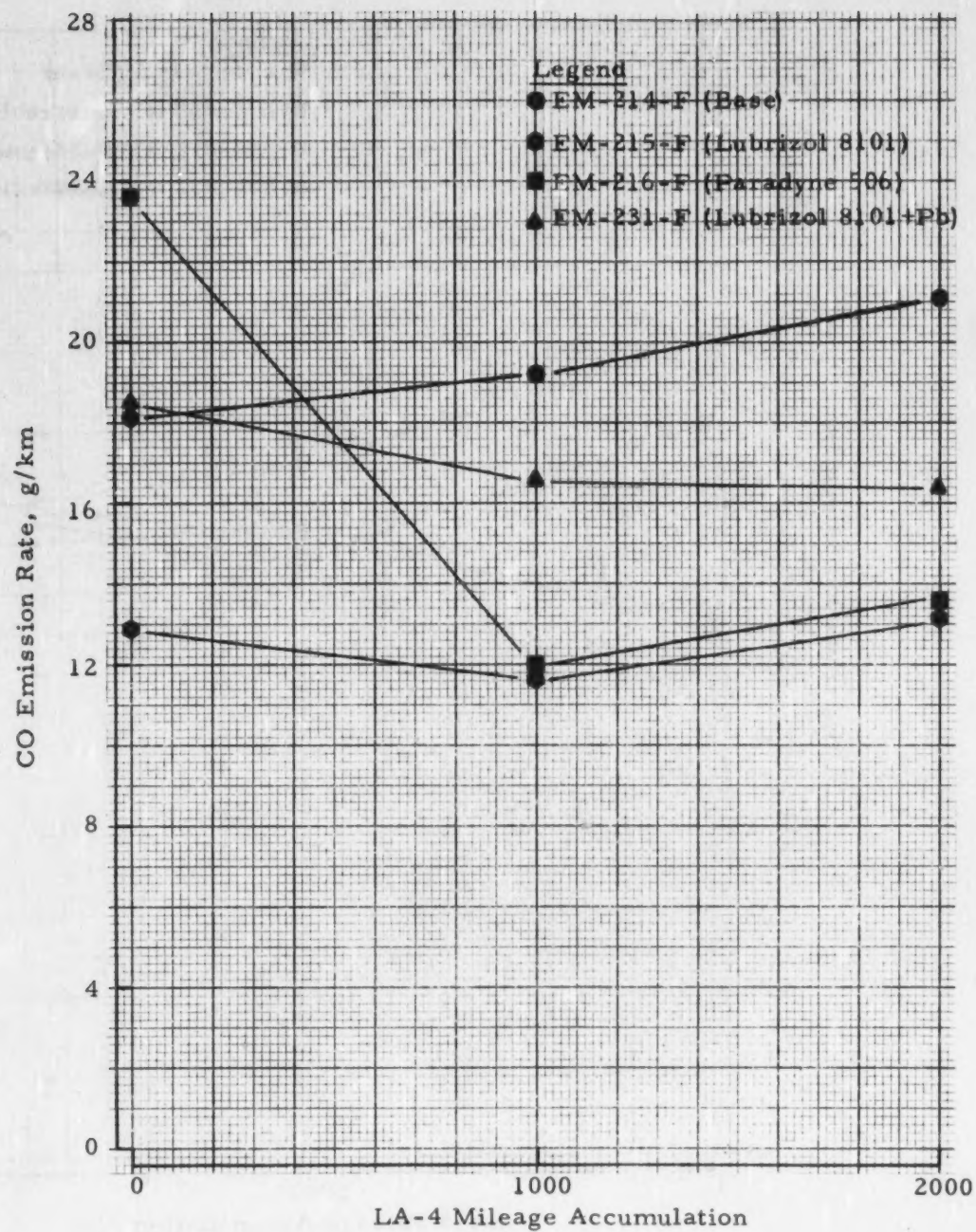


FIGURE 4. CO EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

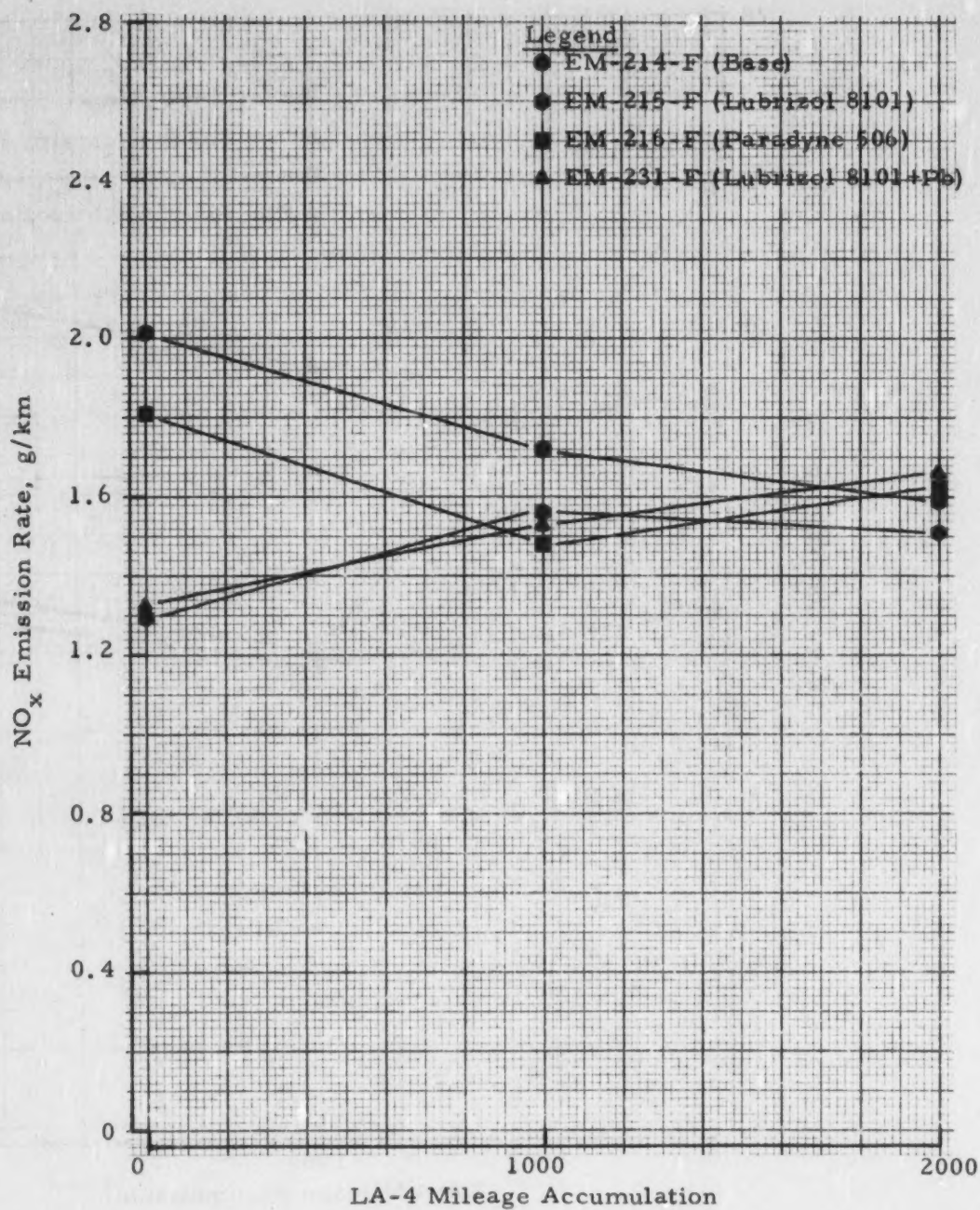


FIGURE 5. NO_x EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

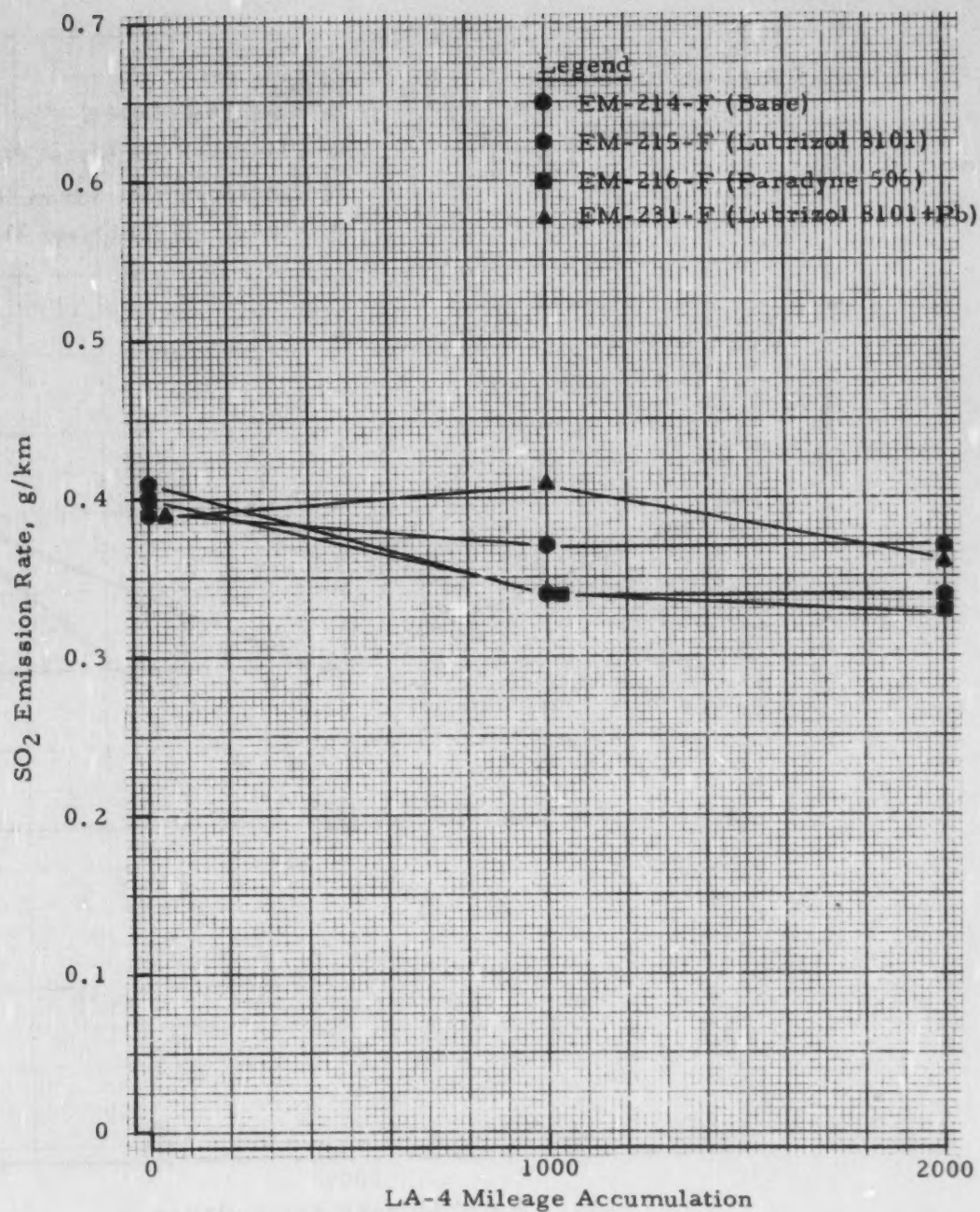


FIGURE 6. SO₂ EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

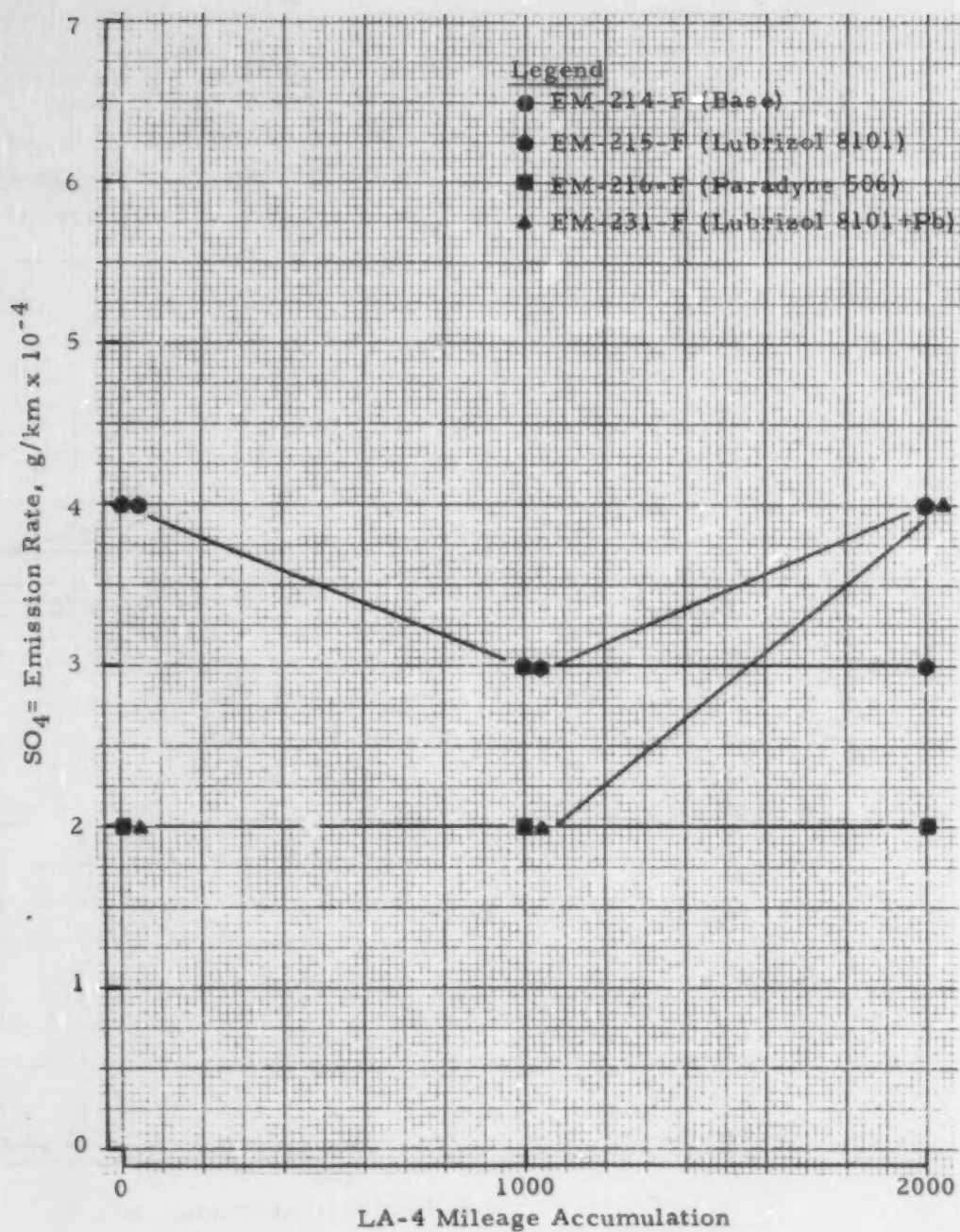


FIGURE 7. $\text{SO}_4=$ EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

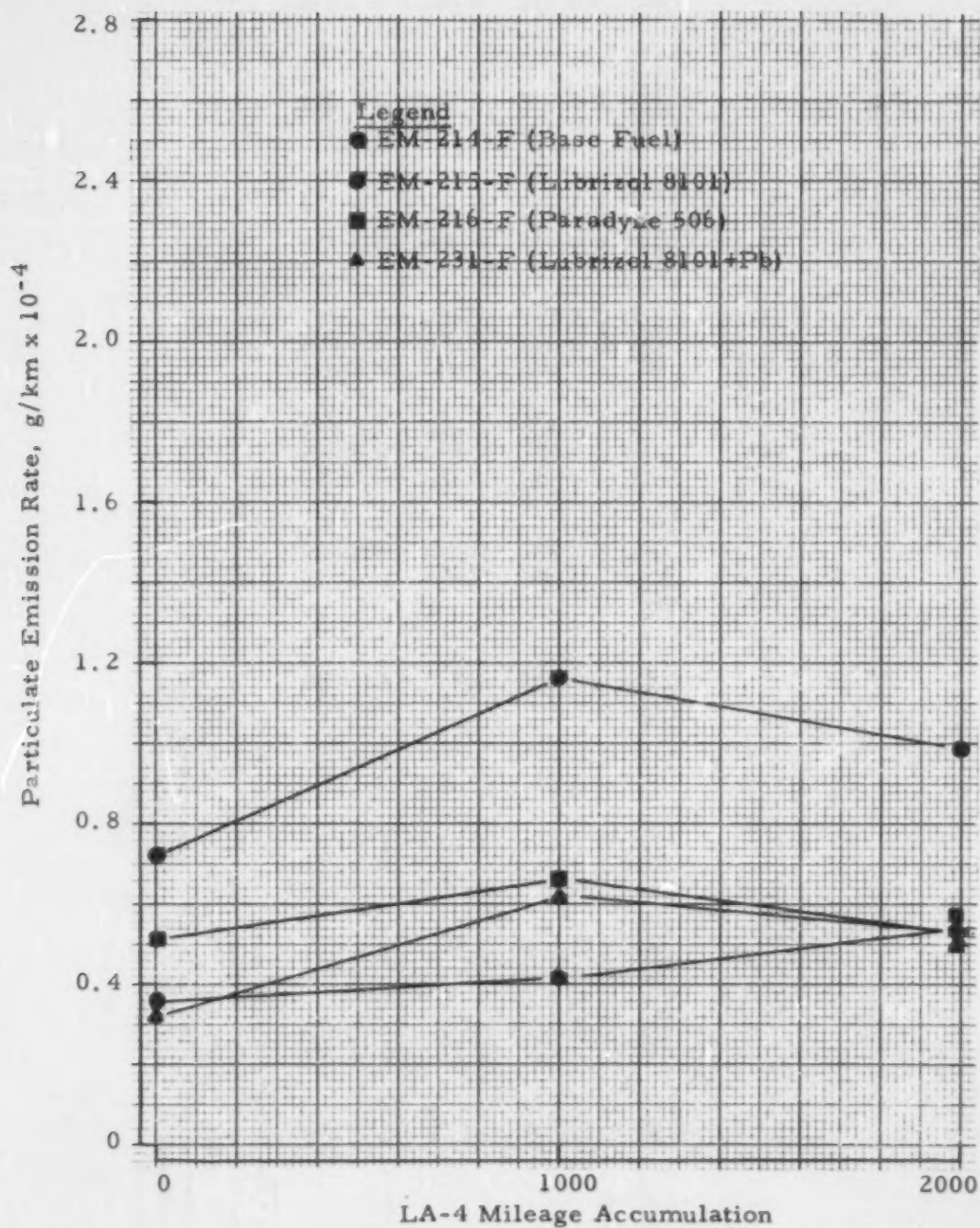


FIGURE 8. PARTICULATE EMISSION RATES OF 1972 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

TABLE 8. SUMMARY OF EXHAUST EMISSIONS OF 1972 CHEVROLET 350 CID ENGINE
EM-215-F (BASE FUEL at 0.1% S + 0.378 g/gal LUBRIZOL 8101)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC(1) HC	SO ₂ (b)(2) SO ₂ (c)	SO ₄ = (3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**			
0 miles	2/10/75	1	1.12	0.16	15.01	1.44	0.30	0.42	0.0004	0.0041	0.10
		2	0.94	0.14	11.66	1.47	0.30	0.38	0.0004	0.0036	0.12
		3	0.92	---	12.22	1.26	0.31	0.38	0.0004	0.0029	0.12
		Avg.	0.99	0.15	12.96	1.39	0.30	0.39	0.0004	0.0035	0.11
1000 miles	2/13/75	1	0.73	0.12	11.29	1.67	0.30	0.38	0.0003	0.0062	0.06
		2	0.77	0.12	11.90	1.45	0.30	0.36	0.0002	0.0021	0.11
		Avg.	0.75	0.12	11.60	1.56	0.30	0.37	0.0003	0.0041	0.08
2000 miles	2/18/75	1	0.78	0.15	14.68	1.52	0.30	0.38	0.0003	0.0072	0.05
		2	0.75	0.12	12.02	1.52	0.27	0.36	0.0003	0.0048	0.06
		3	0.78	---	12.71	1.48	0.33	0.37	0.0003	0.0038	0.08
		Avg.	0.77	0.14	13.14	1.51	0.30	0.37	0.0003	0.0053	0.06

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄ = /particulate indicates the fraction of SO₄ = in the particulate

rates was observed, from 1.39 to 1.51 g/km, with increasing mileage accumulation, as illustrated in Figure 5.

SO₂ (bag) emission rates remained constant at 0.30 g/km while the SO₂ continuous emission rates were about 0.38 g/km for all the test intervals. The sulfate emission rates ranged from 0.3-0.4 mg/km while the particulate emission rates increased from an initial level of 3.5 to 5.3 mg/km at 2000 miles. Sulfur dioxide, sulfate and particulate emission rates as a function of mileage inspection interval is presented in Figures 6, 7, and 8 respectively.

The characterization of the exhaust for various sulfur and nitrogen compounds of interest is presented in Table C-2 of Appendix C. As in the previous test, the only sulfur or nitrogen compound of interest that was detected on a routine basis was nitromethane. The CH₃NO₂ concentration in the first and third bags ranged from 0.18 to 0.31 ppm while the second bag ranged from 0.12 to 0.15 ppm. No ammonia, dimethylnitrosamine, hydrogen sulfide, carbonyl sulfide, methyl or ethyl mercaptan was detected. Individual non-reactive and several reactive hydrocarbons were measured during these tests, and these results are presented in Table B-2 of Appendix B.

The ratio of NRHC/HC ranged from 0.15 to 0.18 over the three emission inspections. The ratio of SO₂ (bag)/SO₂ (continuous) varied between 0.77 and 0.81 for the three test intervals. The fraction of SO₄⁼ in the total particulate decreased from 0.11 to 0.06 from the 0 to 2000 mile inspection.

The sulfur distribution in the exhaust for the 1972 engine using EM-215-F is presented in Table D-2. Sulfur balances using the SO₂ values obtained from the bag samples averaged 108 percent recovery, while using continuous SO₂ values, the sulfur recoveries averaged 134 percent. Less than 0.1 percent of the fuel sulfur appeared as sulfate in the exhaust.

3. EM-216-F Base Fuel, 0.1 Percent Sulfur with 0.486 g/gal Paradyne 506

The third fuel/additive package had 0.486 g/gal Paradyne 506 added to the base fuel doped to 0.1 percent sulfur with thiophene. The results of the individual emission tests are found in Table 9 and these results are summarized in Table 7.

As with the previous tests, the HC emission rates decreased with increasing mileage accumulation, from 1.35 to 0.83 g/km. There was a significant decrease in the CO emission rates, from 23.62 at the initial test to 11.85 and 13.30 g/km at the 1000- and 2000-mile emissions inspection. The effect of mileage accumulation on HC and CO emission rates is presented in Figures 3 and 4. The NO_x emission rate varied between 1.81 and 1.48 g/km over the three test intervals, as illustrated in Figure 5.

TABLE 9. SUMMARY OF EXHAUST EMISSIONS OF 1972 CHEVROLET 350 CID ENGINE
EM-216-F (BASE FUEL at 0.1% S + 0.486 g/gal PARADYNE 506)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***					NRHC(1) HC	SO ₂ (b) ⁽²⁾		SO ₄ = ⁽³⁾ Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**	SO ₂ (c)	SO ₂ (c)	
0 miles	1/10/75	1	1.37	0.25	24.33	1.63	0.29	0.38	0.0002	0.0050	0.01
		2	1.33	0.24	22.91	1.98	0.33	0.42	0.0002	0.0051	0.01
		Avg.	1.35	0.25	23.62	1.81	0.31	0.40	0.0002	0.0051	0.01
1000 miles	1/13/75	1	0.97	0.12	12.80	1.50	0.26	0.35	0.0002	0.0072	0.03
		2	0.95	0.11	10.89	1.45	0.28	0.32	0.0001	0.0059	0.02
		Avg.	0.96	0.12	11.85	1.48	0.27	0.34	0.0002	0.0066	0.03
2000 miles	1/20/75	1	0.84	0.16	13.71	1.53	0.28	0.30	0.0002	0.0050	0.04
		2	0.81	0.13	12.60	1.69	0.29	0.33	0.0002	0.0039	0.05
		3	0.83	---	13.60	1.58	0.30	0.36	0.0002	0.0067	0.03
		Avg.	0.83	0.15	13.30	1.60	0.29	0.33	0.0002	0.0052	0.04

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emissions tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄ = /particulate indicates the fraction of SO₄ = in the particulate

The SO_2 (bag) emission rates ranged from 0.27 to 0.31 g/km while the SO_2 (continuous) emission rate ranged from 0.40 at the 0-mile test to 0.33 g/km at the 2000-mile inspection, as shown in Figure 6. The sulfate emission rate remained at 0.2 mg/km for all three mileage interval tests, as illustrated in Figure 7. The particulate emission rate for EM-216-F ranged only from 5.1 to 6.6 mg/km at the three mileage emission inspections and is shown in Figure 8.

The fraction of NRHC in the total HC ranged from 0.12 to 0.18 at the three test intervals. The fraction of $\text{SO}_4^{=}$ in the total particulate of the 1972 engine operating on EM-216-F increased from 0.01 to 0.04. The SO_2 (bag)/ SO_2 (continuous) ratio ranged from 0.78 to 0.88.

As with the two previous tests, CH_3NO_2 was the only sulfur or nitrogen compound consistently detected, although trace quantities of H_2S and COS were observed upon occasion. The CH_3NO_2 concentrations were slightly higher at the 0- and 2000-mile tests than the two previous fuel/additive tests. The individual bag analysis for all sulfur and nitrogen compounds is presented in Table C-3 of Appendix C.

Sulfur recoveries based on SO_2 bag values were more encouraging than with the two previous fuels. The overall sulfur recovery averaged 95 percent using the SO_2 bag values compared to 115 percent recovery using the continuous SO_2 concentrations. Again, the fraction of fuel sulfur appearing as sulfate in the non-catalyst 1972 engine was less than 0.1 percent. The sulfur distribution for each individual run on the 1972 350 CID Chevrolet engine operating on EM-216-F is presented in Table D-3 of Appendix D.

4. EM-231-F Base Fuel, 0.1 Percent Sulfur, 0.378 g/gal Lubrizol 8101, and 0.05 g/gal TEL

The final fuel additive package evaluated using the 1972 engine was EM-231-F. This was the EPA supplied base fuel doped to a 0.1 percent sulfur level with thiophene. Also added to the fuel was Lubrizol 8101 at 0.378 g/gal and tetra ethyl lead (TEL) motor mix at 0.05 g/gal. As with the previous tests, emission inspections were conducted at the 0-, 1000-, and 2000-mile intervals.

The results of the individual emission tests are presented in Table 10 and are summarized in Table 7. There was only a slight decrease in the HC emission rates over the three inspections as illustrated in Figure 3. The CO emission rates had an insignificant decrease from 18.40 g/km at the initial inspection to about 16.5 g/km at the 1000- and 2000-mile emission tests. There was no definite trend in the NO_x emission rate as a function of mileage accumulation using fuel EM-231-F, as shown in Figure 5.

TABLE 10. SUMMARY OF EXHAUST EMISSIONS OF 1972 CHEVROLET 350 CID ENGINE
EM-231-F (BASE FUEL at 0.1% S + 0.05 g Pb/gal + 0.378 g/gal LUBRIZOL 8101)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***					NRHC(1) HC	SO ₂ (b)(2) SO ₂ (c)	SO ₄ =(3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)* SO ₂ (c)**			
0 miles	3/11/75	1	1.02	0.18	17.91	1.34	0.25	0.0001	0.64	0.03
		2	1.01	0.19	18.89	1.29	0.25	0.0002	0.64	0.06
		Avg.	1.02	0.19	18.40	1.32	0.25	0.0002	0.64	0.05
1000 miles	3/14/75	1	0.88	0.16	16.71	1.41	0.30	0.0002	0.73	0.02
		2	0.91	0.16	17.24	1.71	0.35	0.0001	0.85	0.02
		3	0.87	---	15.93	1.53	0.34	0.0002	0.85	0.05
		Avg.	0.89	0.16	16.63	1.55	0.33	0.0002	0.80	0.03
2000 miles	3/21/75	1	0.88	0.17	16.41	1.34	0.21	0.0002	0.60	0.04
		2	0.93	0.18	16.80	1.47	0.23	0.0004	0.64	0.07
		3	0.82	---	15.87	1.32	0.23	0.0007	0.61	0.14
		Avg.	0.88	0.18	16.36	1.38	0.22	0.0004	0.61	0.08

* SO₂(b) indicates SO₂ values obtained using CVS bag samples
 ** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO
 *** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates
 (2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values
 (3) SO₄/particulate indicates the fraction of SO₄ in the particulate

The SO_2 continuous values ranged from 0.36 to 0.41 g/km. The SO_2 continuous emission rates as a function of mileage accumulation is shown in Figure 6. The $\text{SO}_4^{=}$ emission rates increased from 0.2 mg/km at the initial and 1000-mile emissions inspection to 0.4 mg/km at the final inspection. Particulate emission rates at the three emissions inspections are presented in Figure 8.

The fraction of NRHC/HC ranged from 0.18-0.19 at all three mileage intervals. The ratio of SO_2 (b) / SO_2 (c) was observed to be 0.80 at the 1000-mile emissions inspection compared to about 0.6 at the initial and final tests. The fraction of sulfate in the total particulate ranged from 0.03 at the 1000-mile test to 0.08 at the final inspection.

Individual non-reactive and several reactive hydrocarbon concentrations are presented in Table B-4 of Appendix B to supplement characterization data. Individual sulfur and nitrogen concentrations are presented in Table C-4 of Appendix C. The first and third bag concentrations ranged from 0.23 to 0.40 ppm CH_3NO_2 for all tests with the second bag CH_3NO_2 values ranging between 0.11 and 0.16 ppm. No other sulfur or nitrogen compounds were detected using EM-231-F.

The sulfur distribution for all runs at the three emissions inspections are presented in Table D-4 of Appendix D. This was first fuel/additive package where the sulfur recoveries were less than 85 percent using SO_2 bag values. When using SO_2 continuous concentrations, the sulfur recoveries were higher than the three previous test fuels. Sulfur recoveries at the three inspections ranged from 133 to 142 percent. As with the three previous tests, the fuel sulfur appearing as $\text{SO}_4^{=}$ was less than 0.1 percent on this non-catalyst equipped 1972 Chevrolet 350 engine.

B. 1975 350 CID Chevrolet Engine

The second test stand was a 1975 350 CID Chevrolet engine, equipped with EGR, air pump and GM (AC) pelleted type oxidation catalyst. As with the 1972 engine discussed earlier, emission inspection tests were conducted at 0, 1000, and 2000 miles. The first three fuel/additive packages were identical to those tested on the 1972 version of the 350 CID Chevrolet engine. The final fuel was a high aromatic fuel at the same 0.1 percent sulfur level with Lubrizol 8101. Documentation photos of piston crown and cylinder head deposits were obtained for all fuel/additive combinations. Due to the similarity in appearance of engine deposits, only the 1972 engine deposits are presented.

1. EM-214-F Base Fuel with 0.1 Percent Sulfur

The initial test on the 1975 engine was with the base fuel, EM-214-F. The hot start 1975 LD FTP emission rates for each test at the

three mileage emissions inspection is presented in Table 11 and summarized in Table 12. The HC emission rate increased from about 0.10 g/km at the initial test to 0.26 g/km at the final 2000-mile emissions inspection. The effect of mileage accumulation on the HC emission rates is presented in Figure 9. The CO emission rates increased from 1.75 to 3.12 g/km, as shown in Figure 10. The NO_x emission rates remained relatively constant over the three emission test intervals, as illustrated in Figure 11.

The SO₂ continuous emission rates increased from an initial value of 0.19 to about 0.25 g/km at the 1000- and 2000-mile tests. The effect of mileage accumulation of the SO₂ continuous emission rates of the 1975 engine operating on EM-214-F is presented in Figure 12. The sulfate emission rates are plotted as a function of mileage test interval and are presented in Figure 13. The sulfate emission rates ranged from 6-14 mg/km over the three inspections. Particulate emission rates at the three mileage accumulation test intervals are shown in Figure 14. The particulate emission rate almost doubled between the 1000- and 2000-mile tests.

The substantial increase in HC emission rates at the 2000-mile test was also apparent in the NRHC/HC ratio. The initial and 1000-mile emission tests had NRHC/HC ratios in excess of 0.7, whereas at 2000 miles this dropped to 0.4, which was more consistent with data obtained later in the program. The SO₂ (bag) emission rates were about 70 percent of the SO₂ emission rates obtained using continuous measurement. Typical sulfur recoveries from the fuel sulfur (based on continuous SO₂ and SO₄⁻) ranged from 78 to 96 percent. It is expected that the lower sulfur recoveries on the catalyst engine were due to sulfate and SO₂ storage in the catalyst. The fraction of SO₄⁻ in the total particulate varied from about 0.3 to 0.4.

In addition to the regulated emissions of HC, CO, and NO_x, and the species of specific interest, i.e., SO₂, SO₄, and particulate, characterization of exhaust samples was also obtained for a number of nitrogen and sulfur compounds. Of these compounds, only CH₃NO₂ was found to be present on a consistent basis. Concentrations in the first and third bags ranged from 0.05 to 0.14 ppm while the second bag values ranged from undetected to 0.04. Individual run results for sulfur and nitrogen compounds are presented in Table C-5 of Appendix C.

No ammonia, dimethylnitrosamine, carbonyl sulfide, hydrogen sulfide, or mercaptans were detected in any of the samples. During the measurement of NRHC, a number of individual non-reactive and reactive hydrocarbons were obtained and the results for these runs are presented as additional characterization information as Table B-5 of Appendix B.

It became apparent that sulfate storage would be an important factor in establishing sulfur balances using a catalyst equipped engine.

TABLE 11. SUMMARY OF EXHAUST EMISSIONS OF 1975 CHEVROLET 350 CID ENGINE
EM-214-F (BASE FUEL at 0.1% S)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC(1) HC	SO ₂ (b)(2) SO ₂ (c)	SO ₄ =(3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**			
0 miles	12/17/74	1	0.10	0.08	1.67	1.08	0.14	0.21	0.0219	0.67	0.43
		2	0.09	0.06	1.82	1.25	0.14	0.17	0.0273	0.82	0.36
		Avg.	0.10	0.07	1.75	1.17	0.14	0.19	0.0246	0.75	0.40
1000 miles	12/20/74	1	0.09	0.06	2.03	1.37	0.15	0.24	0.0196	0.63	0.35
		2	0.07	0.08	2.26	1.30	0.19	0.25	0.0256	0.76	0.23
		Avg.	0.08	0.07	2.15	1.34	0.17	0.25	0.0226	0.70	0.29
2000 miles	12/30/74	1	0.26	0.11	3.11	1.33	0.15	0.28	0.0149	0.54	0.40
		2	0.27	0.10	3.12	1.22	0.17	0.21	0.0133	0.81	0.31
		Avg.	0.26	0.11	3.12	1.28	0.16	0.24	0.0141	0.68	0.36

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄=/particulate indicates the fraction of SO₄ in the particulate

TABLE 12. SUMMARY OF 1975 350 CID CHEVROLET ENGINE EMISSION RATES

Exhaust Species	1975 LD FTP (Hot Start) Emission Rate, g/km											
	EM-214-F			EM-215-F			EM-216-F			EM-218-F		
	0	1000	2000	0	1000	2000	0	1000	2000	0	1000	2000
HC	0.10	0.08	0.26	0.12	0.10	0.09	0.17	0.18	0.15	0.11	0.09	0.11
NRHC	0.07	0.07	0.11	0.05	0.06	0.05	0.05	0.06	0.05	0.05	0.05	0.04
NRHC/HC	0.73	0.91	0.40	0.46	0.43	0.49	0.31	0.31	0.34	0.44	0.48	0.37
CO	1.75	2.15	3.12	1.97	1.68	1.34	4.64	2.41	2.39	1.46	1.41	1.01
NO _x	1.17	1.34	1.28	0.97	1.18	1.31	1.03	1.35	1.62	0.87	1.16	1.26
SO ₂ (b)	0.14	0.17	0.16	0.26	0.19	0.23	0.20	0.23	0.18	0.21	0.22	0.17
SO ₂ (c)	0.19	0.25	0.24	0.31	0.29	0.30	0.32	0.30	0.26	0.25	0.24	0.20
SO ₂ (b)/SO ₂ (c)	0.75	0.70	0.68	0.84	0.67	0.77	0.61	0.76	0.68	0.85	0.91	0.88
SO ₄ *	9.7	6.4	14.1	9.7	14.1	21.8	2.8	8.0	10.1	22.0	22.3	30.0
Part.*	24.6	22.6	39.5	29.7	41.3	35.2	17.2	25.7	21.4	57.8	58.7	76.7
SO ₄ =/Part.	0.40	0.29	0.36	0.32	0.34	0.38	0.18	0.30	0.45	0.38	0.38	0.39

* mg/km

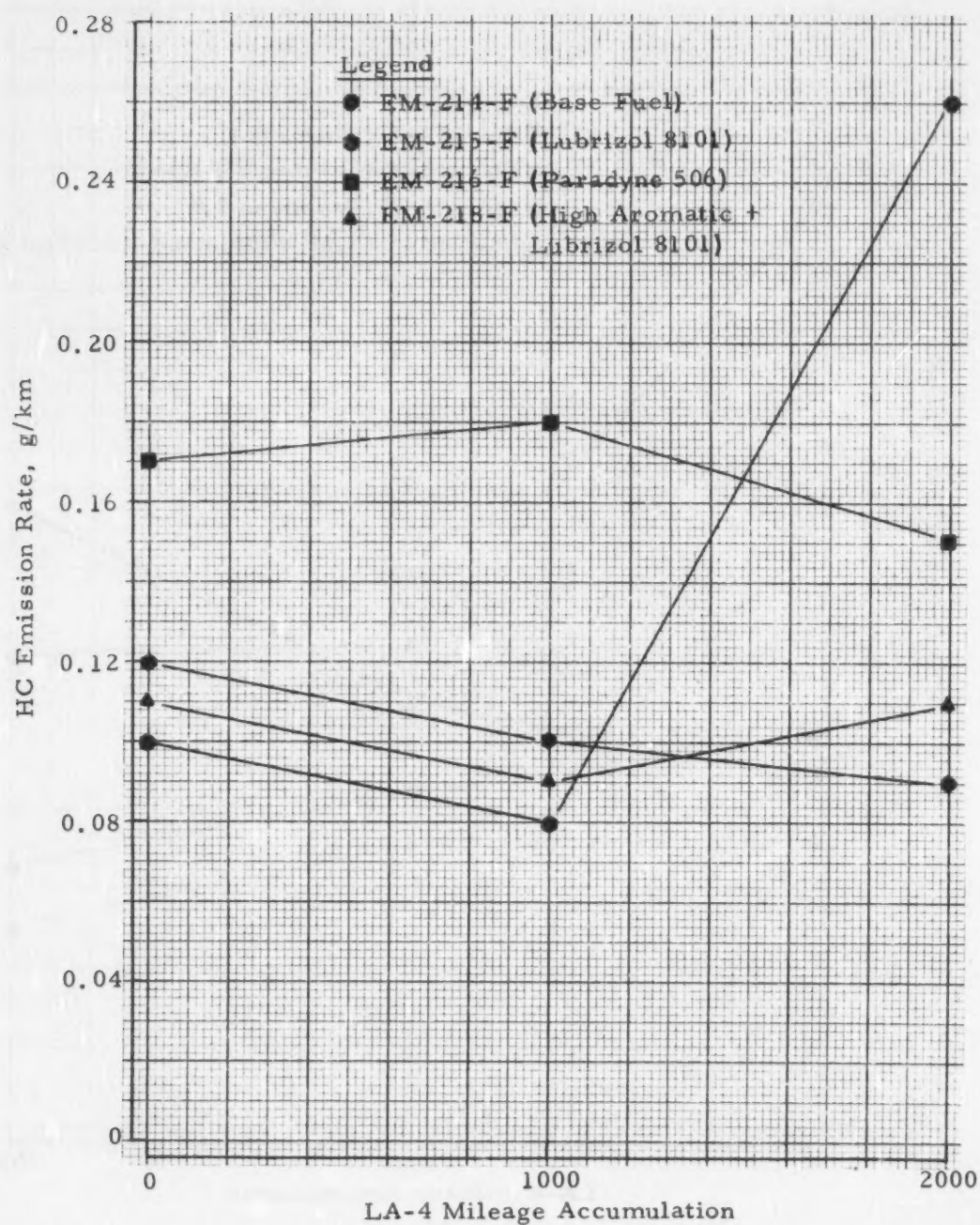


FIGURE 9. HC EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

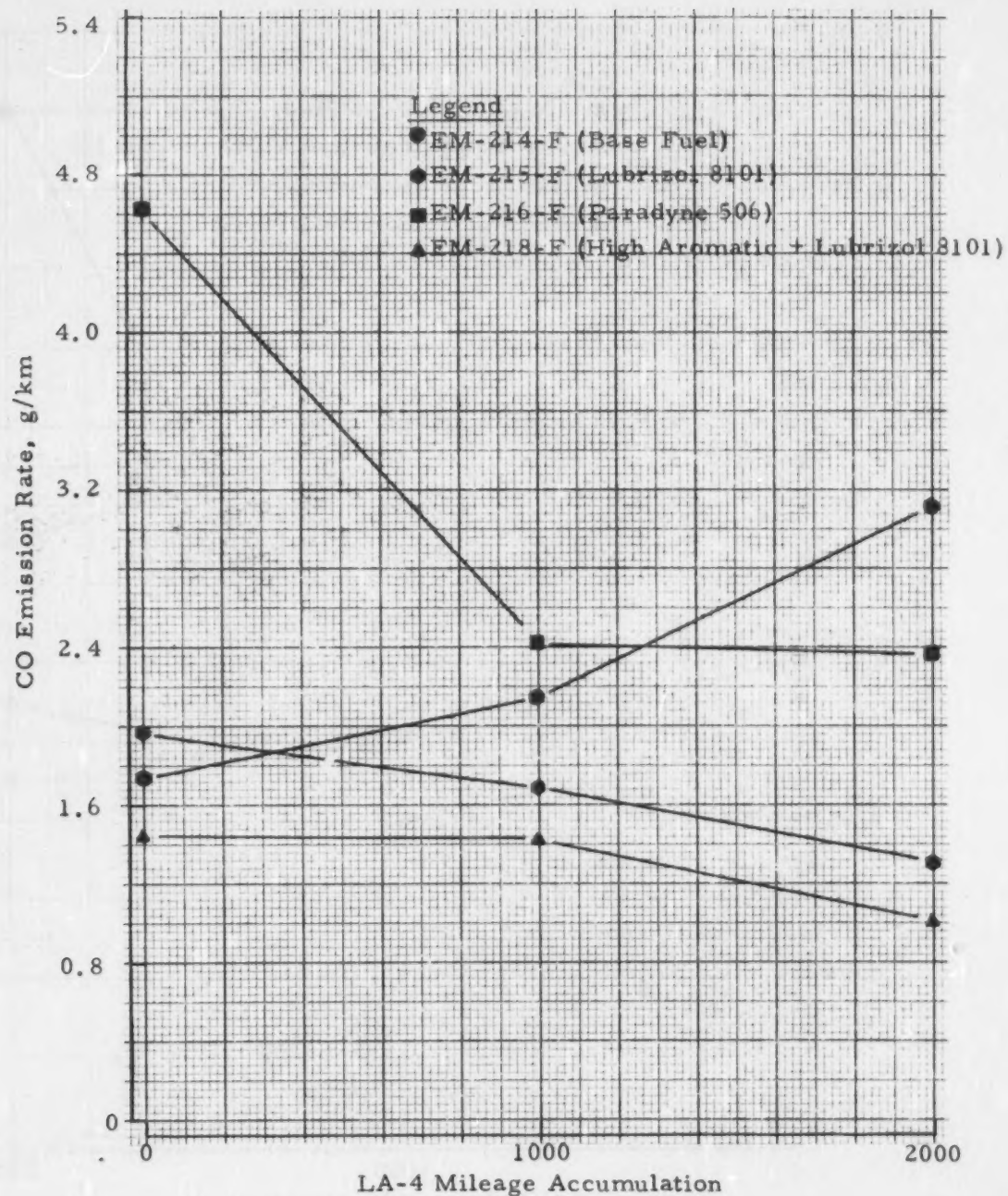


FIGURE 10. CO EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

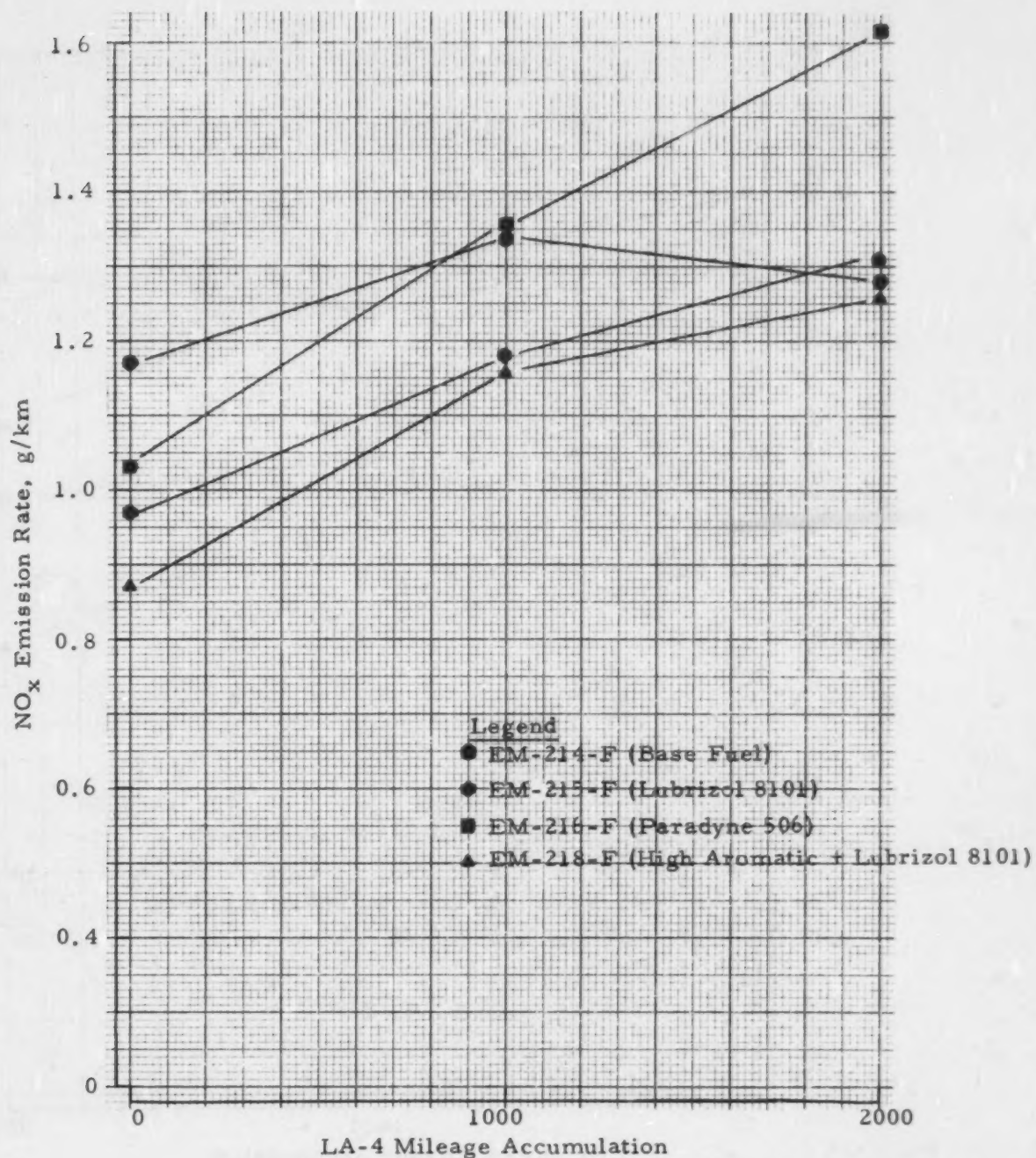


FIGURE 11. NO_x EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

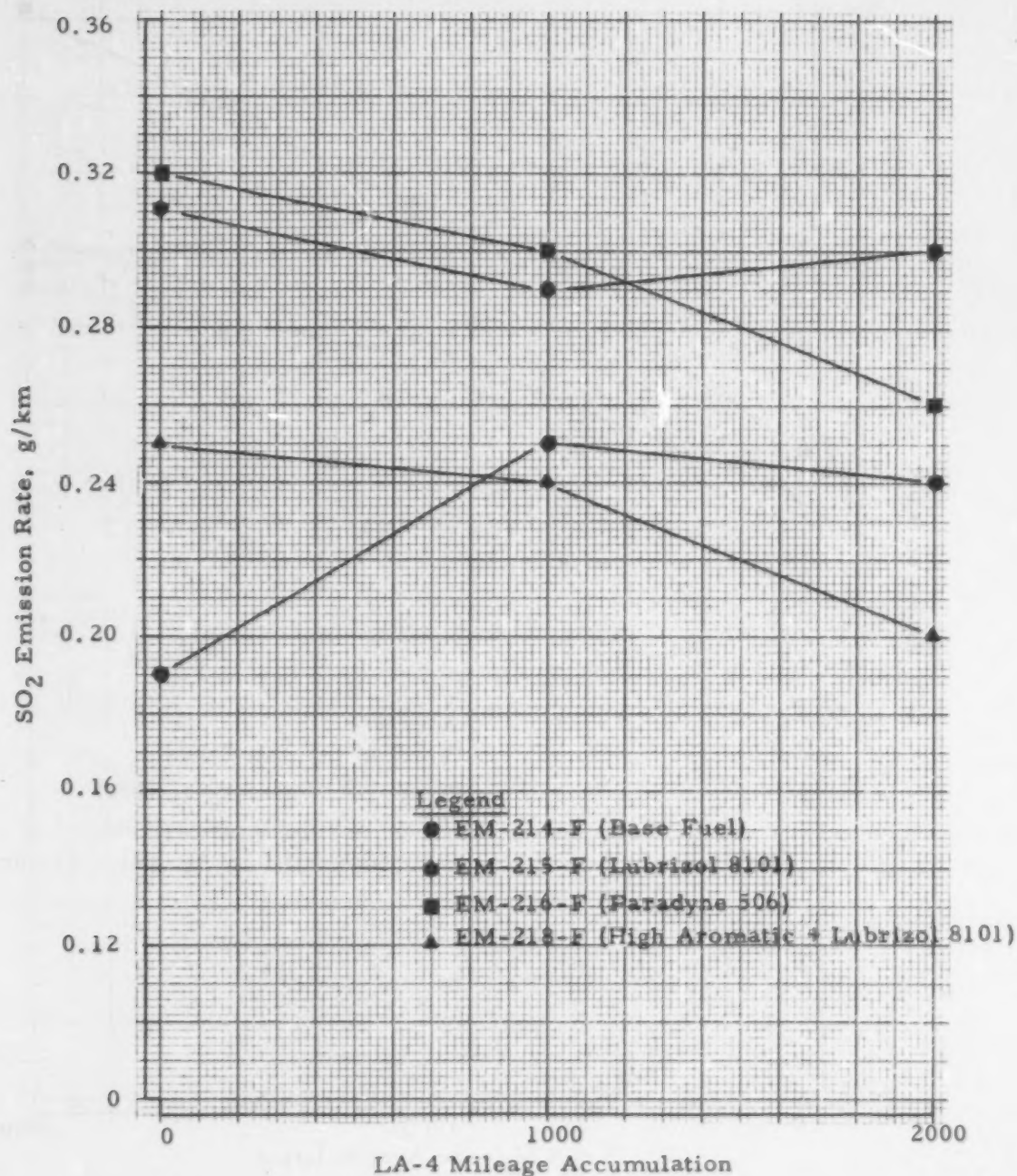


FIGURE 12. SO₂ EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

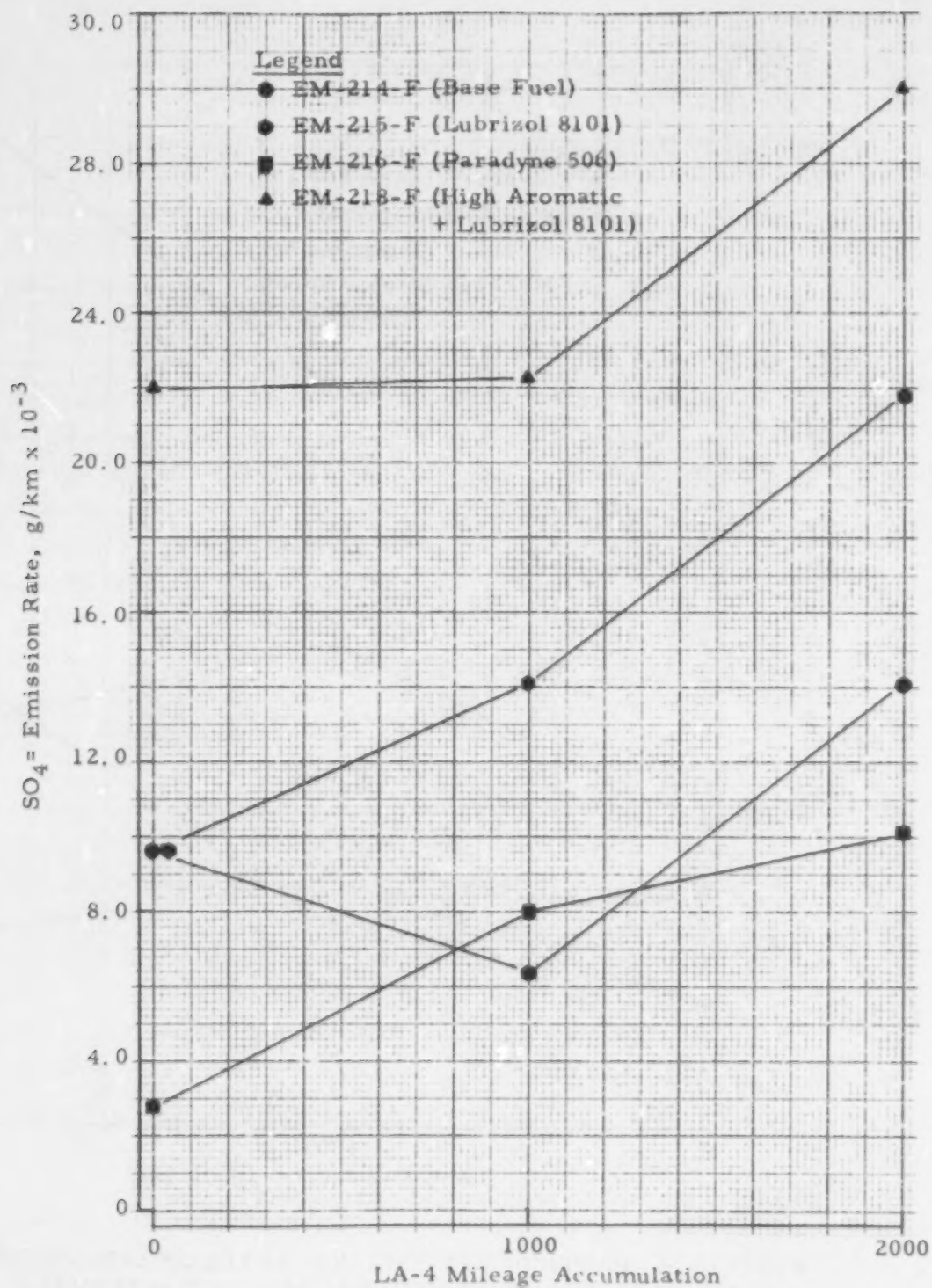


FIGURE 13. SO₄= EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

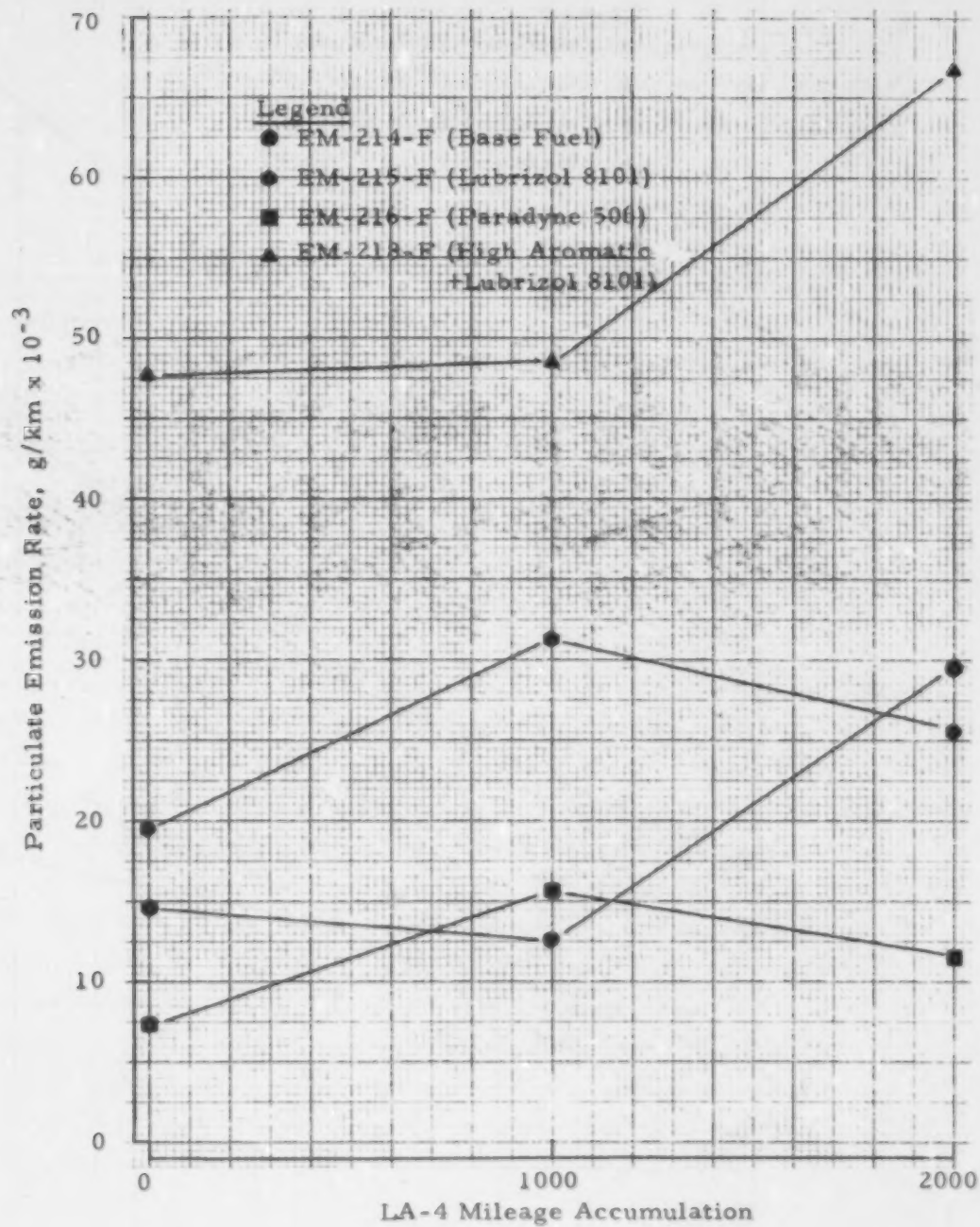


FIGURE 14. PARTICULATE EMISSION RATES OF 1975 350 CID CHEVROLET ENGINE AT SEVERAL MILEAGE INTERVALS WITH THE FOUR TEST FUELS

Sulfur recoveries based on SO_2 continuous readings ranged from 78 to 96 percent. The percent of fuel sulfur appearing as sulfate was 2-4 percent. Individual run results are presented in Table D-5 of Appendix D.

2. EM-215-F Base Fuel, 0.1 Percent S, 0.378 g/gal Lubrizol 8101

Another fuel/additive package used in the characterization of emissions of the 1975 350 CID Chevrolet engine was Lubrizol 8101. The base fuel at a 0.1 percent sulfur level had Lubrizol 8101 added at 0.378 g/gal. The results of each individual run at all three of the emissions inspections is presented in Table 13 and summarized in Table 12.

The HC emission rates decreased from 0.12 g/km at the initial test to 0.09 g/km at the 2000-mile emissions inspection. The CO emission rates decreased with increasing mileage accumulation as illustrated in Figure 10. An increase in the NO_x emission rate was observed, from 0.97 g/km at the 0-mile test to 1.31 g/km at the final 2000 mile inspection. The effect of mileage accumulation on the NO_x emission rates of the 1975 engine operating on EM-215-F is shown in Figure 11.

The SO_2 (continuous) emission rates remained essentially constant at about 0.30 g/km over the three test inspections. The sulfate emission rates as a function of mileage accumulation are shown in Figure 13. As observed, there was a gradual increase in the $\text{SO}_4^{=}$ emission rates over the mileage accumulation schedule. The particulate emission rates ranged from 30 to 41 mg/km, and the emission rates as a function of mileage accumulation are illustrated in Figure 14. The SO_2 (bag) emission rates were 67 to 84 percent of the continuous SO_2 emission rates. The NRHC/HC ratio remained relatively constant ranging between 0.43 and 0.49. The ratio of sulfate fraction in the total particulate mass also remained stable ranging only from 0.32 to 0.38, slightly increasing with mileage.

The individual results of sulfur and nitrogen compound are presented in Table D-6 of Appendix D. As with the previous tests on the 1975 engine, the only species present during the emission testing was the nitromethane. The first and third bag concentration ranged from 0.09 to 0.32 ppm, with no apparent trend as a function of mileage accumulation. Individual non-reactive and several reactive hydrocarbon concentration are presented in Table B-6 of Appendix B for characterization data for the three bags at the three emission inspection intervals. Sulfur distribution in the exhaust for all runs using EM-215-F in the 1975 engine is presented in Table D-6 of Appendix D. Sulfur recoveries based on continuous SO_2 concentrations averaged 109 percent for the three emissions inspections.

TABLE 13. SUMMARY OF EXHAUST EMISSIONS OF 1975 CHEVROLET 350 CID ENGINE
EM-215-F (BASE FUEL at 0.1% S + 0.378 g/gal LUBRIZOL 8101)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC ⁽¹⁾ HC	SO ₂ (b) ⁽²⁾ SO ₂ (c)	SO ₄ = ⁽³⁾ Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)**	SO ₂ (c)**			
0 miles	2/7/75	1	0.12	0.05	1.70	0.99	0.28	0.28	0.42	1.00	0.31
		2	0.10	0.05	1.96	0.98	0.23	0.31	0.50	0.74	0.29
		3	0.14	---	2.26	0.74	0.28	0.35	---	0.80	0.36
		Avg.	0.12	0.05	1.97	0.97	0.26	0.31	0.46	0.84	0.32
1000 miles	2/14/75	1	0.14	0.06	1.43	1.30	0.18	0.28	0.43	0.64	0.31
		2	0.12	0.05	1.61	1.07	0.19	0.28	0.42	0.68	0.38
		3	0.14	---	2.00	1.18	0.21	0.23	---	0.70	0.35
		Avg.	0.10	0.06	1.68	1.18	0.19	0.29	0.43	0.67	0.34
2000 miles	2/17/75	1	0.09	0.05	1.45	1.51	0.20	0.29	0.56	0.69	0.41
		2	0.12	0.05	1.41	1.26	0.24	0.30	0.42	0.80	0.40
		3	0.10	---	0.96	1.26	0.25	0.30	---	0.83	0.37
		4	0.06	---	1.52	1.21	0.24	0.32	---	0.75	0.33
		Avg.	0.09	0.05	1.34	1.31	0.23	0.30	0.49	0.77	0.38

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄ = / particulate indicates the fraction of SO₄ = in the particulate

3. EM-216-F, 0.1 Percent Sulfur with 0.468 g/gal Paradyne 506

Another fuel/additive package contained 0.468 g/gal Paradyne 506 in the base fuel at a 0.1 percent sulfur level. The individual emission rates for all runs at the three inspections are presented in Table 14 and summarized in Table 12. The HC emission rates changed only slightly with increasing mileage, as shown in Figure 9. The CO emission rate at the initial inspection was 4.64 g/km and decreased to 2.4 g/km at the 1000- and 2000-mile tests, as shown in Figure 10. The NO_x emission rates increased from 1.03 g/km at the 0-mile inspection to 1.62 g/km at the final emission test.

The SO₂ (continuous) emission rates decreased from 0.32 g/km to 0.26 over the three test intervals. The effect of mileage accumulation on the SO₂ (continuous) emission rates is shown in Figure 12. The sulfate emission rates increased from 2.8 to 10.1 mg/km, as shown in Figure 13. The particulate emission rates ranged from 17.2 to 25.7 g/km.

The fraction of SO₂ (bag) / SO₂ (continuous) ranged from 0.61 at the initial inspection to 0.76 at the 1000-mile tests. The NRHC/HC ratio varied only slightly during the 2000 miles of operation, ranging between 0.31 and 0.34. The fraction of sulfate in the total particulate increased with increasing mileage accumulation. At the initial inspection, the fraction was only 0.18 and increased to 0.30 and 0.45 at the 1000- and 2000-mile inspections, respectively.

The measurement of individual nitrogen and sulfur compounds was conducted on all three bags at the three emissions inspection intervals. The results of these tests are presented in Table C-7 of Appendix C to assist in the characterization of the exhaust. In addition, individual non-reactive and several reactive hydrocarbons measured during these same tests are presented in Table B-7 of Appendix B.

The sulfur distribution for the 1975 engine operating on EM-216-F is presented in Table D-7 of Appendix D for all tests. The percent fuel sulfur appearing as SO₂ (continuous) varied from 90-110 percent. The percent fuel sulfur appearing as sulfate increased from 1.1 to 2.5 with increasing mileage accumulation.

4. EM-218-F High Aromatic, 0.1 Percent Sulfur, 0.378 g/gal Lubrizol 8101

The final fuel/additive package contained 0.378 g/gal Lubrizol 8101 in a high aromatic fuel doped with thiophene to a 0.1 percent sulfur level. The emission rates for each run at the three inspections is found in Table 15 and summarized in Table 12. The HC emission rates remained essentially constant at 0.1 g/km at the three test intervals, as shown in Figure 9.

TABLE 14. SUMMARY OF EXHAUST EMISSIONS OF 1975 CHEVROLET 350 CID ENGINE
EM-216-F (BASE FUEL at 0.1% S + 0.486 g/gal PARADYNE 506)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC ⁽¹⁾ HC	SO ₂ (b) ⁽²⁾ SO ₂ (c)	SO ₄ [±] (3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**			
0 miles	1/9/75	1	0.14	0.05	6.23	1.17	0.22	0.33	0.0146	0.67	0.09
		2	0.17	0.05	3.53	0.88	0.18	0.31	0.0129	0.58	0.12
		3	0.19	---	4.15	1.05	0.19	0.32	0.0242	0.59	0.33
		Avg.	0.17	0.05	4.64	1.03	0.20	0.32	0.0172	0.61	0.18
1000 miles	1/14/75	1	0.18	0.06	2.70	1.29	0.21	0.29	0.0181	0.72	0.27
		2	0.17	0.05	2.13	1.41	0.24	0.30	0.0333	0.80	0.33
		Avg.	0.18	0.06	2.41	1.35	0.23	0.30	0.0257	0.76	0.30
2000 miles	1/17/75	1	0.16	0.05	2.57	1.63	0.18	0.25	0.0087	0.72	0.41
		2	0.14	0.05	2.20	1.61	0.17	0.27	0.0115	0.63	0.48
		Avg.	0.15	0.05	2.39	1.62	0.18	0.26	0.0101	0.68	0.45

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emission tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄[±]/particulate indicates the weight fraction of SO₄[±] in the particulate

TABLE 15. SUMMARY OF EXHAUST EMISSIONS OF 1975 CHEVROLET 350 CID ENGINE
EM-218-F (HIGH AROMATIC FUEL at 0.1% S + 0.378 g/gal LUBRIZOL 8101)

Mileage Interval	Date	Run No.	1975 LD FTP Emission Rate, g/km***						NRHC(1) HC	SO ₂ (b)(2) SO ₂ (c)		SO ₄ = (3) Part.
			HC	NRHC	CO	NO _x	SO ₂ (b)*	SO ₂ (c)**				
0 miles	3/10/75	1	0.12	0.05	1.47	0.82	0.23	0.25	0.0187	0.0512	0.92	0.37
		2	0.11	0.05	1.57	0.85	0.23	0.27	0.0261	0.0666	0.85	0.39
		3	0.10	---	1.35	0.94	0.17	0.22	0.0213	0.0558	0.77	0.38
		Avg.	0.11	0.05	1.46	0.87	0.21	0.25	0.0220	0.0578	0.85	0.38
1000 miles	3/17/75	1	0.10	0.04	1.52	1.16	0.22	0.23	0.0178	0.0476	0.96	0.37
		2	0.09	0.05	1.30	1.15	0.21	0.25	0.0274	0.0730	0.84	0.38
		3	0.09	---	1.41	1.16	0.22	0.24	0.0216	0.0556	0.92	0.39
		Avg.	0.09	0.05	1.41	1.16	0.22	0.24	0.0223	0.0587	0.91	0.38
2000 miles	3/20/75	1	0.12	0.04	1.04	1.29	0.18	0.20	0.0258	0.0670	0.90	0.39
		2	0.10	0.04	1.02	1.26	0.16	0.18	0.0316	0.0800	0.89	0.40
		3	0.11	---	0.98	1.24	0.18	0.21	0.0327	0.0831	0.86	0.39
		Avg.	0.11	0.04	1.01	1.26	0.17	0.20	0.0300	0.0767	0.88	0.39

* SO₂(b) indicates SO₂ values obtained using CVS bag samples

** SO₂(c) indicates SO₂ values obtained using continuous on-line sampling with TECO

*** All 1975 LD FTP emissions tests are conducted using hot starts

(1) NRHC/HC indicates the ratio of NRHC to HC emission rates

(2) SO₂(b)/SO₂(c) indicates the ratio of bag SO₂ to continuous SO₂ values

(3) SO₄=/particulate indicates the fraction of SO₄= in the particulate

The CO emission rates were about 1.4 g/km for the first two inspections and decreased to 1.0 g/km at the final test interval. The effect of mileage accumulation on the NO_x emission rates of the 1975 engine operating on EM-218-F is presented in Figure 11. As illustrated, the NO_x emission rates increased from 0.87 g/km at the 0-mile test to 1.26 g/km at the final 2000-mile test.

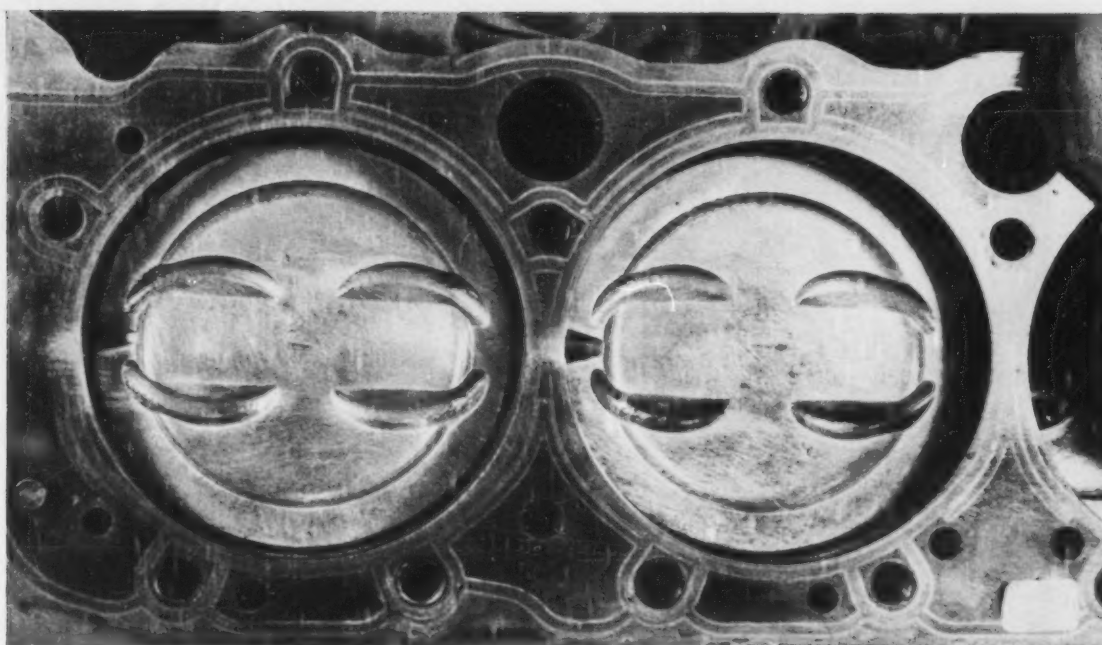
The SO₂ continuous emission rates decreased from 0.25 g/km at the initial test to 0.20 g/km at the 2000-mile emissions inspection. The effect of mileage accumulation on the SO₂ continuous emission rates is illustrated in Figure 12. Sulfate emission rates remained at 22 mg/km for the first two emissions inspection (0 and 1000 miles) and increased to 30 mg/km at 2000 miles, as shown in Figure 13. Similar results were observed for particulate emission rates in that the first two emission test intervals produced about 58 mg/km while the final test resulted in a particulate emission rate of 77 mg/km. Figure 14 illustrates the effect of mileage accumulation on particulate emissions.

The fraction of NRHC in the total hydrocarbons varied between 0.37 and 0.48 for the three emission inspections. The ratio of SO₂ (bag)/SO₂ (continuous) at a nominal 0.88 for the same tests. The sulfate fraction of the total particulate remained essentially constant at 0.38. The sulfur distribution for each run is presented in Table D-8 of Appendix D. Sulfur recoveries from this high aromatic fuel were the best of all fuel/additive combinations. This was the only test fuel where the SO₂ continuous recoveries were less than 100 percent.

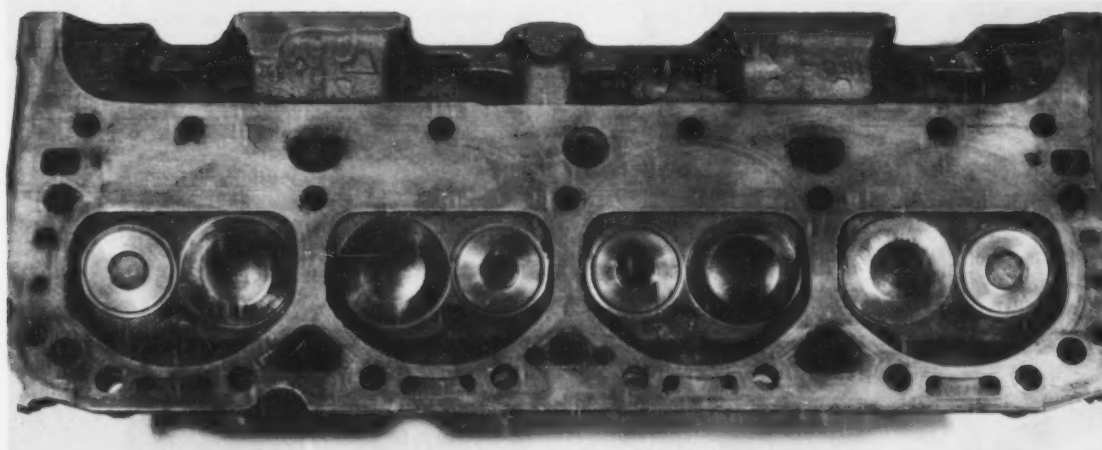
C. Documentation of Engine Deposits

During the initial phase of the program, it was decided to obtain documentation photos of the piston head, cylinder head, and valve deposits of both engines. These documentation photos were obtained prior to engine cleanup and the deposits represent approximately 2000 miles of repetitive LA-4 cycles. Photos of typically cleaned piston heads and cylinder heads are illustrated in Figure 15. The piston deposits for all four test fuels are shown in Figure 16 for the 1972 350 CID Chevrolet engine. The major difference in the appearance of the piston deposits of the four test fuels was the white deposits observed with EM-231-F. This was the only fuel/additive package which contained lead. The remainder of the piston deposits were black in color and were generally of a crisp, flaky nature.

Cylinder head deposits for the four fuel/additive packages for the 1972 350 CID Chevrolet engine are presented in Figure 17. The base fuel EM-214-F cylinder head deposits are slightly lighter in color than either of the two fuel/additive packages (EM-215-F and EM-216-F). The final fuel/additive package containing lead had a substantial increase in the quantity of white deposits on the cylinder head. It is assumed that these

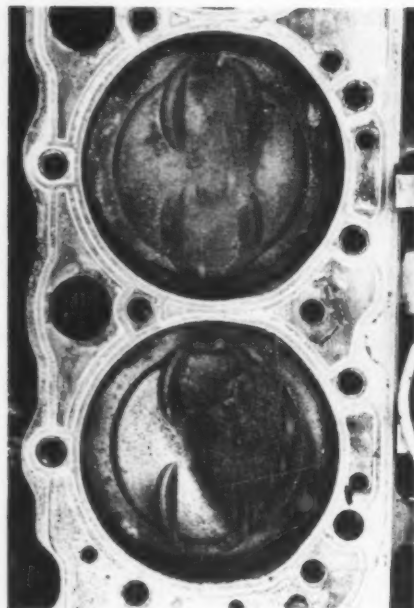


Cleaned Piston Heads

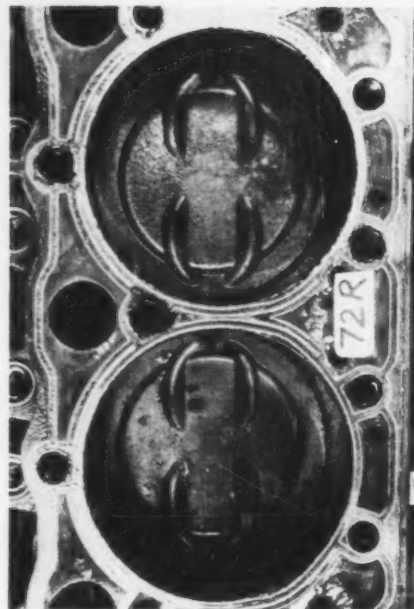


Cleaned Cylinder Heads

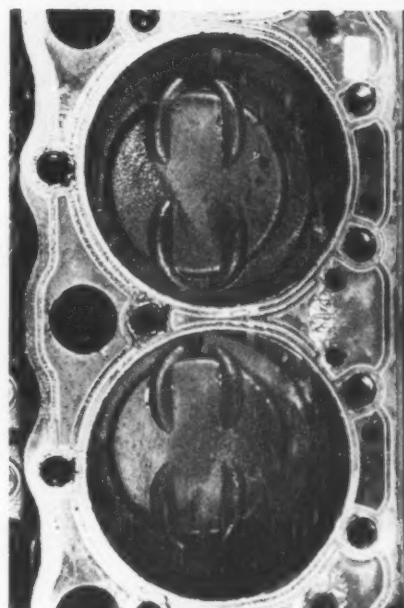
FIGURE 15. TYPICALLY CLEANED PISTON HEADS AND
CYLINDER HEADS, 1972 CHEVROLET 350 ENGINE



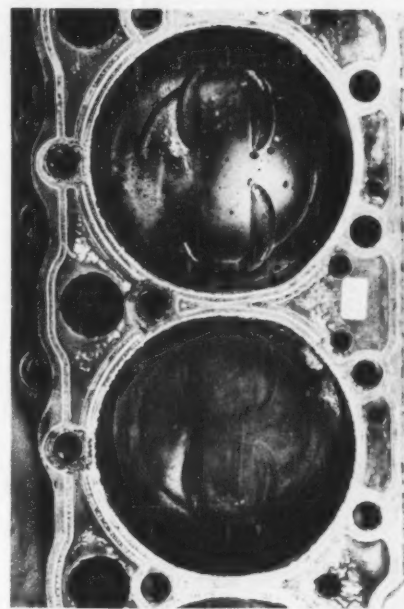
EM-214-F, Base Fuel at 0.1 Percent Sulfur



EM-215-F, Base Fuel at 0.1 Percent Sulfur with 0.378 g/gal Lubrizol 8101

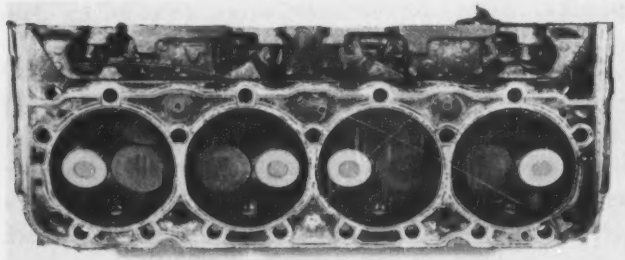


EM-216-F, Base Fuel at 0.1 Percent Sulfur with 0.486 g/gal Paradyne 506

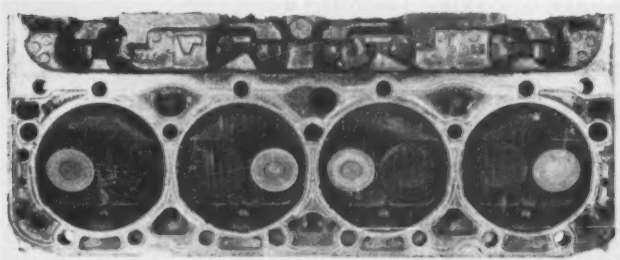


EM-213-F, Base Fuel at 0.1 Percent Sulfur with 0.378 g/gal Lubrizol 8101 and 0.05 g/gal TEL

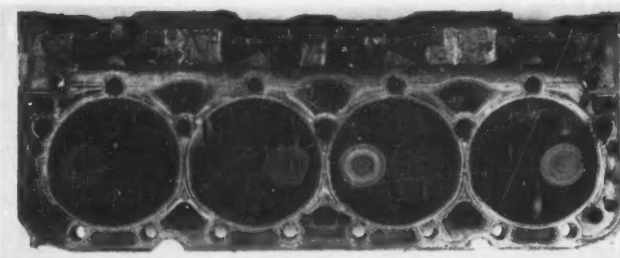
FIGURE 16. TYPICAL PISTON DEPOSITS FROM 1972 350 CID CHEVROLET ENGINE OPERATING ON THE FOUR TEST FUELS AFTER 2000 MILES OF LA-4 CYCLES



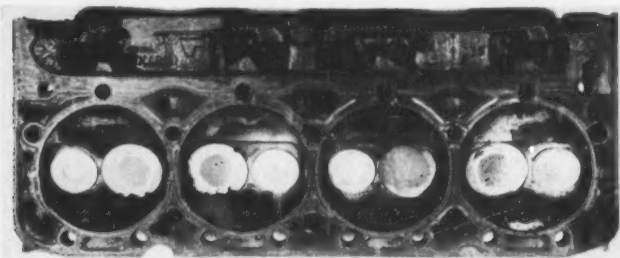
EM-214-F, Base Fuel at 0.1 Percent Sulfur



EM-215-F, Base Fuel at 0.1 Percent Sulfur with 0.378 g/gal Lubrizol



EM-216-F, Base Fuel at 0.1 Percent Sulfur with 0.486 g/gal Paradyne 506



EM-213-F, Base Fuel at 0.1 Percent Sulfur
with 0.378 g/gal Lubrizol 8101 and 0.05 g/gal TEL

FIGURE 17. CYLINDER HEAD DEPOSITS OF 1972 350 CID CHEVROLET ENGINE
OPERATING THE FOUR TEST FUELS AT 2000 MILES OF LA-4 CYCLES

are lead salt deposits, since no further work regarding their composition was performed.

Valve deposit documentation was obtained for the three final fuel/additive packages. Figure 18 represents typically cleaned valves and the valve deposits that were observed after 2000 miles of repetitive LA-4 cycles. As observed, a significant amount of intake valve deposits were found with all three fuel/additive packages. However, it should be pointed out that although documentation photos were not obtained using the base fuel, visual inspection of the valves indicated little difference between base fuel and the fuel/additive packages.

The base fuel was supplied without any additives, and between the initial analysis by the supplier and completion of the final test fuel, the ASTM D-381 existent gum values had doubled. Documentation photos of the 1975 350 CID Chevrolet engine piston and cylinder head were obtained, but the similarity of deposit characteristics for the four fuels did not warrant inclusion in this report.

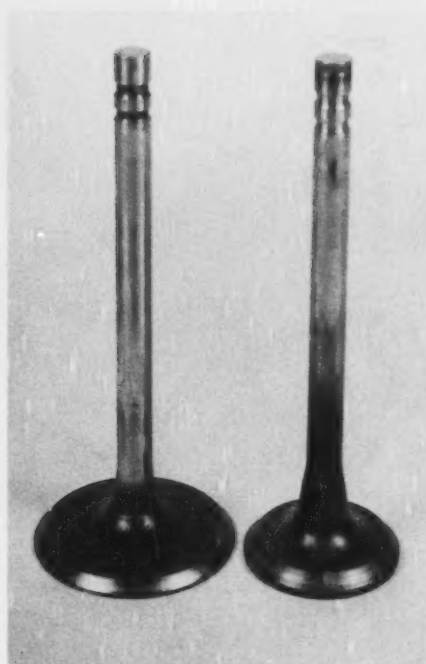
Although the scope of work for this program did not include deposit documentation, it was felt that this could be considered an important factor in the characterization as a function of fuel and additive composition. Future work may want to consider looking for differences in engine deposits as a function of fuel/additive packages.

D. Statistical Analysis

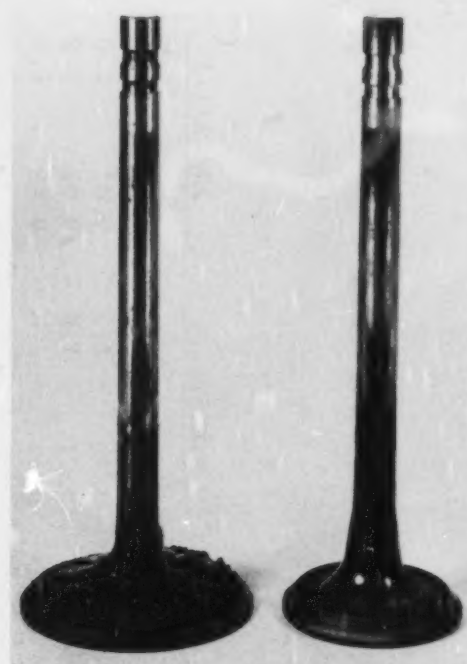
The amount of emissions rate data generated during the course of the program provided a basis for statistical analysis. This data was obtained during the program and examination of this data from a statistical standpoint is "after-the-fact". The design of the experiment was not such that statistical analysis of the data was of primary concern. It is, however, an important aspect that should not be overlooked.

The use of the two engine configurations provided an opportunity to make comparisons of emission testing standard deviation (S_x) and standard deviation in percent of mean value ($\% S_x$). Preliminary experiments were conducted during the emission qualification testing phase using hot starts and during the full scale emission testing. Generally, two four-emission tests were conducted during the full scale testing; and consequently, the data presented must be viewed accordingly. Table 16 illustrates the S_x and $\% S_x$ values determined on the 1972 350 CID Chevrolet engine for all four fuels. The S_x and $\% S_x$ values found for the 1975 engine are presented in Table 17.

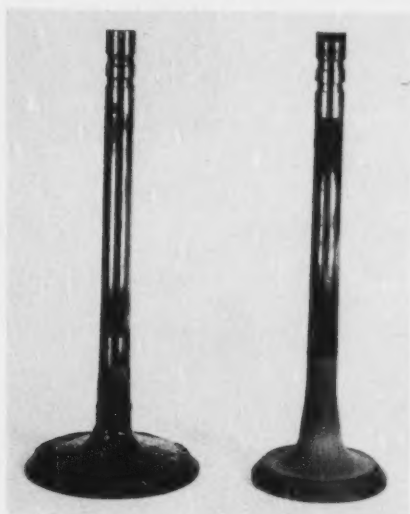
A summary of the S_x and $\% S_x$ values from the full-scale testing, initial "hot start" qualification testing, and standard certification values



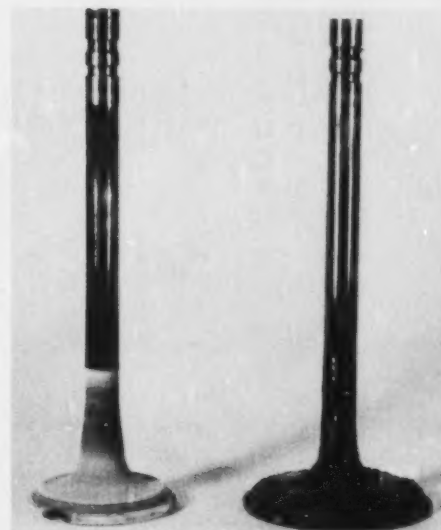
Typically Cleaned Valves



EM-216-F, Base Fuel at 0.1 Percent Sulfur
with 0.486 g/gal Paradyne 506



EM-215-F, Base Fuel at 0.1 Percent
Sulfur with 0.378 g/gal Lubrizol 8101



EM-231-F, Base Fuel at 0.1 Percent
Sulfur with 0.378 g/gal Lubrizol 8101
and 0.05 g/gal TEL

FIGURE 18. TYPICALLY CLEANED VALVES AND VALVE DEPOSITS FROM
1972 350 CID CHEVROLET ENGINE OPERATING ON THREE TEST FUELS
WITH 2000 MILES OF LA-4 CYCLES

TABLE 16. STANDARD DEVIATION (S_x) AND STANDARD DEVIATION
IN PERCENT OF MEAN VALUE ($\% S_x$) FOR
1972 350 CID CHEVROLET ENGINE
WITH ALL FOUR TEST FUELS

Emission	Miles	EM-214-F		EM-215-F		EM-216-F		EM-231-F	
		S_x	$\% S_x$	S_x	$\% S_x$	S_x	$\% S_x$	S_x	$\% S_x$
HC	0	0.21	13.2	0.11	11.1	0.03	2.2	0.01	1.0
HC	1000	0.09	6.0	0.03	4.0	0.01	1.0	0.02	2.2
HC	2000	0.03	2.1	0.02	2.6	0.02	2.4	0.06	6.8
CO	0	1.00	5.5	1.79	13.8	1.00	4.2	0.69	2.8
CO	1000	1.27	6.6	0.43	3.7	1.35	11.4	0.66	4.0
CO	2000	0.21	1.0	1.38	10.5	0.61	4.6	0.47	2.9
NO _x	0	0.03	1.5	0.11	7.9	0.25	13.8	0.04	3.0
NO _x	1000	0.02	1.2	0.16	10.2	0.04	2.7	0.15	9.7
NO _x	2000	0.04	2.5	0.02	1.3	0.08	5.0	0.08	5.8

1972 350 CID Chevrolet

Average $\% S_x$ for HC = 4.6

Average $\% S_x$ for CO = 6.0

Average $\% S_x$ for NO_x = 5.4

TABLE 17. STANDARD DEVIATION (S_x) AND STANDARD DEVIATION
IN PERCENT OF MEAN VALUE ($\% S_x$) FOR
1975 350 CID CHEVROLET ENGINE
WITH ALL FOUR TEST FUELS

Emission	Miles	EM-214-F		EM-215-F		EM-216-F		EM-218-F	
		S_x	$\% S_x$	S_x	$\% S_x$	S_x	$\% S_x$	S_x	$\% S_x$
HC	0	0.01	10.0	0.02	16.7	0.03	17.6	0.01	9.1
HC	1000	0.01	12.5	0.01	7.7	0.01	5.6	0.01	11.1
HC	2000	0.01	3.8	0.02	22.2	0.01	6.7	0.01	9.1
CO	0	0.11	6.3	0.28	14.2	1.41	30.4	0.11	7.5
CO	1000	0.16	7.4	0.29	17.3	0.40	16.6	0.11	7.8
CO	2000	0.01	0.3	0.25	18.7	0.26	10.9	0.03	3.0
NO _x	0	0.12	10.3	0.03	3.1	0.15	14.6	0.06	6.9
NO _x	1000	0.05	3.7	0.12	10.2	0.08	5.9	0.01	0.9
NO _x	2000	0.08	6.3	0.15	10.7	0.01	0.6	0.03	2.4

1975 350 CID Chevrolet
Average $\% S_x$ for HC = 11.0
Average $\% S_x$ for CO = 11.7
Average $\% S_x$ for NO_x = 6.3

supplied by the Project Officer are presented in Table 18. The % S_x observed from the emission tests conducted during the program indicated a noticeable improvement in the % S_x . The 1972 engine hot start dynamometer test was a much more statistically reliable test procedure based on the standard cold start % S_x . These values were 1/2 to 1/3 of the standard cold start certification tests. The % S_x for the 1975 was slightly better than the standard cold start certification tests. When determining the effects due to the fuel additive on regulated emissions, a number of factors should be considered. The first is the variability of the emissions test itself, and a second consideration should be the deterioration of emissions due to a number of factors. Calculated deterioration factors based on the base fuel run indicate that there were no significant increase in regulated or non-regulated emission rates that could be solely attributed to the fuel additive package.

Using the same rationale employed in the Federal Register, determination of deterioration factors was attempted. It became apparent that there was no deterioration for HC or NO_x and the increase in CO emission rates for the 1972 engine. A similar comparison was made with the 1975 engine but decreases in CO and HC indicate no deterioration during the short mileage accumulation used in this program. After attempting to determine deterioration factors for both engines operating on the base fuel, it became apparent that no deterioration could be observed that could not be explained by the inherent variability of the emissions test procedure.

Hydrocarbon was the only emission which was found to be affected by the fuel additive package. Lower HC emissions were observed with the three fuel additive packages on the 1972 engine than with the base fuel. Other changes in the regulated emission rates can be explained by the emission test variability and variable engine emission deterioration. Statistical analysis of the limited data available on the "worst case" 1975 engine was applied to determine the number of tests required to detect a deterioration of 10 or 25 percent change in emissions due to a fuel additive package, if such an effect were present. The t-test is generally used for testing the difference of two population means when the number of samples are small. This test assumes that the variances (σ) of the two populations are equal. In order to determine the number of tests required, an estimate of $\mu_1 - \mu_2$ is needed (where μ_1 and μ_2 are the population means). For the emissions data on the 1975 350 CID Chevrolet engine, the largest average % S_x was 11.7 for CO for all tests. Using this for estimation purposes yields

$$\frac{\mu_1}{\sigma} \approx 9 \qquad \mu_1 = 9 \sigma$$

TABLE 18. COMPARISON OF STANDARD DEVIATION
IN PERCENT OF MEAN VALUE (% S_x) OF
STANDARD COLD START FTP, HOT START QUALIFICATION
TESTING AND FUEL SCALE HOT START EMISSION TESTING

Emission	Standard Deviation in Percent of Mean Value				
	Standard FTP	Qualification Tests *		Avg. Emission Tests**	
		1972	1975	1972	1975
HC	13.0	4.7	3.6	4.6	11.0
CO	18.2	6.8	25.0	6.0	11.7
NO _x	9.1	3.7	2.9	5.4	6.3

*using "hot start" 1975 FTP testing

**Average of emission inspection test for all four fuels

Assume that μ_2 differs from μ_1 by 10 percent or more; i.e.,

$$|\mu_1 - \mu_2| \geq 0.1 \mu_1 = 0.9 \sigma$$

Assume that the probability of rejecting the hypothesis of no difference when the hypothesis is true is 0.05, commonly referred to as α . Further assume that the probability of accepting the hypothesis of no difference is 0.1, commonly referred to as β . A final assumption is that the baseline (i.e., the emissions from the fuel with no additive) does not change.

In summary,

$$\Delta = \frac{|\mu_1 - \mu_2|}{\sigma} = .9$$

$$\alpha = 0.05$$

$$\beta = 0.1$$

Based on this information and published literature⁽¹⁰⁾, it can be determined that the sample size is 27. This means that 27 tests would be required from both the baseline and fuel additive package.

Using the same reasoning for a deterioration of 25 percent in emissions and assume

$$|\mu_1 - \mu_2| \geq .25 \mu_1$$

then $\Delta = 2.25$ and results in a corresponding sample size of 6. This indicates that six tests would be necessary from both the baseline and the fuel additive package.

IV. SUMMARY AND CONCLUSIONS

The objectives of this project, which were to characterize gaseous emissions as a function of fuel/additive composition and evaluate the usefulness of the 1975 LD FTP as a satisfactory screening procedure, were achieved. Sufficient data has been presented to satisfactorily characterize the two 350 CID Chevrolet engines on four test fuels. Chemical analytical procedures were obtained from EPA-RTP while others were developed by SwRI during the procedural development phase of the research effort. These procedures are described in sufficient detail to allow others to implement them. The two special engine dynamometer test facilities were designed to simulate vehicle operation and to allow mileage accumulation using an automatic tape controlled servo-driver. These test facilities were successfully employed and proved reliable and durable.

Although a substantial amount of baseline characterization data has been generated with the two engines operating on both fuels, a number of findings seem apparent as a result of this research project, and the most important ones are described as follows:

1. Of the various sulfur compounds evaluated, the only ones present in the exhaust of both engines were SO_2 and $\text{SO}_4^{=}$. Hydrogen sulfide, carbonyl sulfide, methyl mercaptan, and ethyl mercaptan were below the limits of detectability for the method of analysis employed in this program. The SO_2 emission rates for the 1972 engine were greater, since the oxidation catalyst on the 1975 engine converted SO_2 to $\text{SO}_4^{=}$ and also stored some SO_2 . Sulfate levels of the 1975 engine were 20 to 100 times those of the non catalyst equipped 1972 engine. Sulfate storage and the relatively light driving cycle of the 1975 LD FTP indicate that this is not a satisfactory test procedure for measuring sulfate. Sulfate accounted for 30-45 percent of the total particulate weight in the 1975 engine as compared to 1-11 percent for the 1972 engine. Of the fuel sulfur, less than 0.1 percent appeared as $\text{SO}_4^{=}$ in the exhaust of the 1972 engine; whereas, 18-45 percent was observed as $\text{SO}_4^{=}$ in the 1975 engine. Additional work is warranted for the measurement of SO_2 , $\text{SO}_4^{=}$, and particulate using a more appropriate test cycle. More work for the analysis of other sulfur compounds should also be conducted if another test cycle is employed and other catalysts and fuel/additive combinations are included.

2. Of the nitrogen compounds evaluated, nitromethane was the only nitrogen compound detected in the exhaust of both engines with all four fuel/additive combinations. No ammonia or dimethylnitrosamine was detected throughout the testing on either engine on any of the four test fuels. There was no significant differences in the concentrations of nitromethane due to the engine configuration or test fuel using the 1975 LD FTP. Additional work may be warranted if an alternative test procedure is proposed or if other fuel/additives, catalysts, or engines are employed.

3. The ability of the 1975 LD FTP to determine the effects of fuel/additive composition on regulated emission rates was found to be marginal. This is not surprising since no specific effort was made to make the 1975 LD FTP discriminate between fuels and fuel additives when it was developed. A substantial procedural development effort, not within the scope of this project, is needed to demonstrate a suitable, discriminatory fuel additive test protocol. The nature of the program required minor engine overhaul at the conclusion of each test fuel and the baseline emission rates were slightly different after each rebuilding. This was particularly true for CO and HC making it difficult to distinguish between engine and fuel additive effects on emissions except on a percent change basis.

Non-reactive hydrocarbons accounted for 15-20 percent of total hydrocarbons in the 1972 engine with no apparent trend as a function of mileage accumulation. Although the fraction of NRHC in the total hydrocarbon varied considerably at the 0- and 1000-mile emission inspection, the results of the 2000-mile inspection with the base fuel was within the range observed with the test fuels; namely, 30-50 percent. No changes in the NRHC/HC were noted for a given fuel/additive package that could be attributed strictly to the test fuel on either engine.

4. Particulate and sulfate were non-regulated emissions where changes in emission rates could be attributed to the fuel/additive package. The high aromatic fuel was observed to produce nominally twice the sulfate and particulate emission rate as the base fuel with the same fuel additive in the 1975 engine. Although EM-231-F was treated with TEL motor mix, the treatment level of 0.05 g/gal should be considered only a trace level; and, consequently, the particulate emission rates from the 1972 engine were not substantially higher than the unleaded fuel additive packages. Since particulate and sulfate emissions appear to be more sensitive to fuel composition than to additive formulation, additional work involving fuel composition effects on sulfate and particulate emissions may be warranted.

5. The engine dynamometer configuration designed to simulate vehicle operation using the 1975 LD FTP was successfully used with both engines for all four test fuels. The automatic driver arrangement was found to be an invaluable aid in the simultaneous mileage accumulation on the two engines. The system was designed to allow substitution of other driving cycles for mileage accumulation. Actual driving for record was accomplished using a manual driver just as is normally done when testing cars on the chassis dynamometer.

6. For the majority of chemical species measured during this program, the 1975 LD FTP was insufficiently sensitive to detect effects due to the fuel additive treatments evaluated. The 1975 LD FTP is basically a light driving schedule, and the problem of sulfate storage could be eliminated by using a more appropriate driving cycle.

7. The relative light driving cycle (1975 LD FTP) for mileage accumulation made the engines prone to intake manifold and valve deposits. These deposits were observed with both additive packages and to a lesser extent with the base fuels.

8. The gaseous emissions variability was improved using the hot start engine dynamometer. Comparison of accepted standard deviation in percent of mean values indicate an improvement in the reliability of the gaseous emissions test procedure.

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APPENDIX A

METHODS OF CHEMICAL ANALYSIS

1. Non-Reactive Hydrocarbons (NRHC)
2. Sulfur Dioxide (SO_2)
3. Sulfate ($\text{SO}_4^{=}$)
4. Nitrogen Compounds
5. Sulfur Compounds

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1. Non-Reactive Hydrocarbons (NRHC)

The measurement of NRHC was performed using a gas chromatograph procedure developed by EPA (RTP)⁽⁸⁾. This procedure uses a single flame ionization detector with a multiple column arrangement and dual gas sampling valves. The timed sequence selection valves allow for the baseline separation of air, CH₄, C₂H₄, C₂H₂, C₃H₈, C₃H₆, C₆H₆, and C₇H₈. Although only CH₄, C₂H₆, C₂H₂, C₃H₈, and C₆H₆ are considered non-reactive, C₂H₄, C₃H₆, and C₇H₈ were determined during the course of the analysis. Only the non-reactive hydrocarbons are used in the calculation of NRHC emission rates, but all individual hydrocarbon data is useful in the characterization of emissions from the two Chevrolet engines.

Samples were obtained directly from the bag samples of 1975 LD FTP and analyzed in the NRHC system. Individual NRHC values were determined and a NRHC value for the bag was calculated. This value was then used to determine the NRHC emission rates for these tests. By knowing the NRHC and HC emission rates, it was possible to determine the fraction of NRHC in the total HC. A detailed description of the individual columns, temperatures, flow rates, etc. may be found in Reference 8. Figure A-1 illustrates the NRHC analytical instrumentation that was used for this analysis.

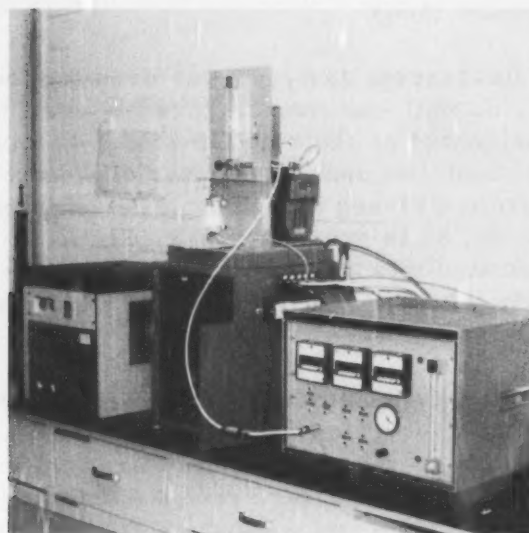


FIGURE A-1. NON-REACTIVE HYDROCARBON
GAS CHROMATOGRAPH INSTRUMENTATION

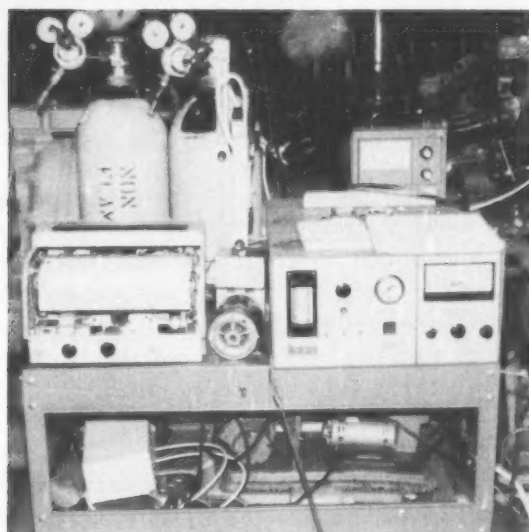


FIGURE A-2. TECO MODEL 40 PULSED
FLUORESCENT SO₂ ANALYZER

2. Sulfur Dioxide (SO₂)

A pulsed fluorescent analyzer was used for the measurement of sulfur dioxide. This unit was manufactured by the Thermo Electron Corporation and is designated as their TECO Model 40 and is shown in Figure A-2. This instrument was used to monitor dilute exhaust both on a continuous basis and from CVS bag samples. The sampling interface used with the TECO Model 40 is presented in Figure A-3. A supplementary pump was incorporated into the system to keep the response time less than three seconds. All sample lines were Teflon, and the use of stainless steel was minimized when possible.

The use of the TECO Model 40 SO₂ instrument required the acquisition of zero and span gases for daily calibration. Since the intended application for this instrument was dilute (air rich) exhaust, the use of air balance SO₂ span gases and air zero was selected for calibration purposes. Although the instrument was advertised not to have interferences, a series of experiments were conducted to verify this. These experiments included various concentrations of CO, NO_x, and HC in N₂, as well as several individual hydrocarbons in N₂ and air. Based on the results of these experiments, it was apparent that a number of potential problems could be avoided provided certain precautions were observed. Best results from the TECO Model 40 were observed when sampling from dilute auto exhaust (without an ice trap) using a fluoropore filter and to use air balance span gases and air zero gas. Even using all of the precautions previously mentioned, the fuel sulfur recoveries consistently exceeded 100 percent throughout the program.

Span gases were named using the procedure supplied by Matheson Gas Products as the method they used to name the cylinders initially. Sulfur dioxide span gases are particularly susceptible to absorption and initially it was difficult to obtain a span gas that would maintain the SO₂ level that it had when received in the lab. By the beginning of the mileage accumulation, SO₂ span gases were in hand that had been sufficiently preconditioned to allow a stable SO₂ concentration.

Although the SO₂ instrument was not totally free of interferences, it was felt that it was the most satisfactory instrument available at that time. During the course of the program, it was found that the bag SO₂ values were consistently lower than the continuous readings. When calculating sulfur balances, the recoveries based on SO₂ continuous values were generally high ranging from 110 to 125 percent in most cases. Based on the experience obtained during this program, it is questionable that this instrument is satisfactory for measuring SO₂ in automotive exhaust.

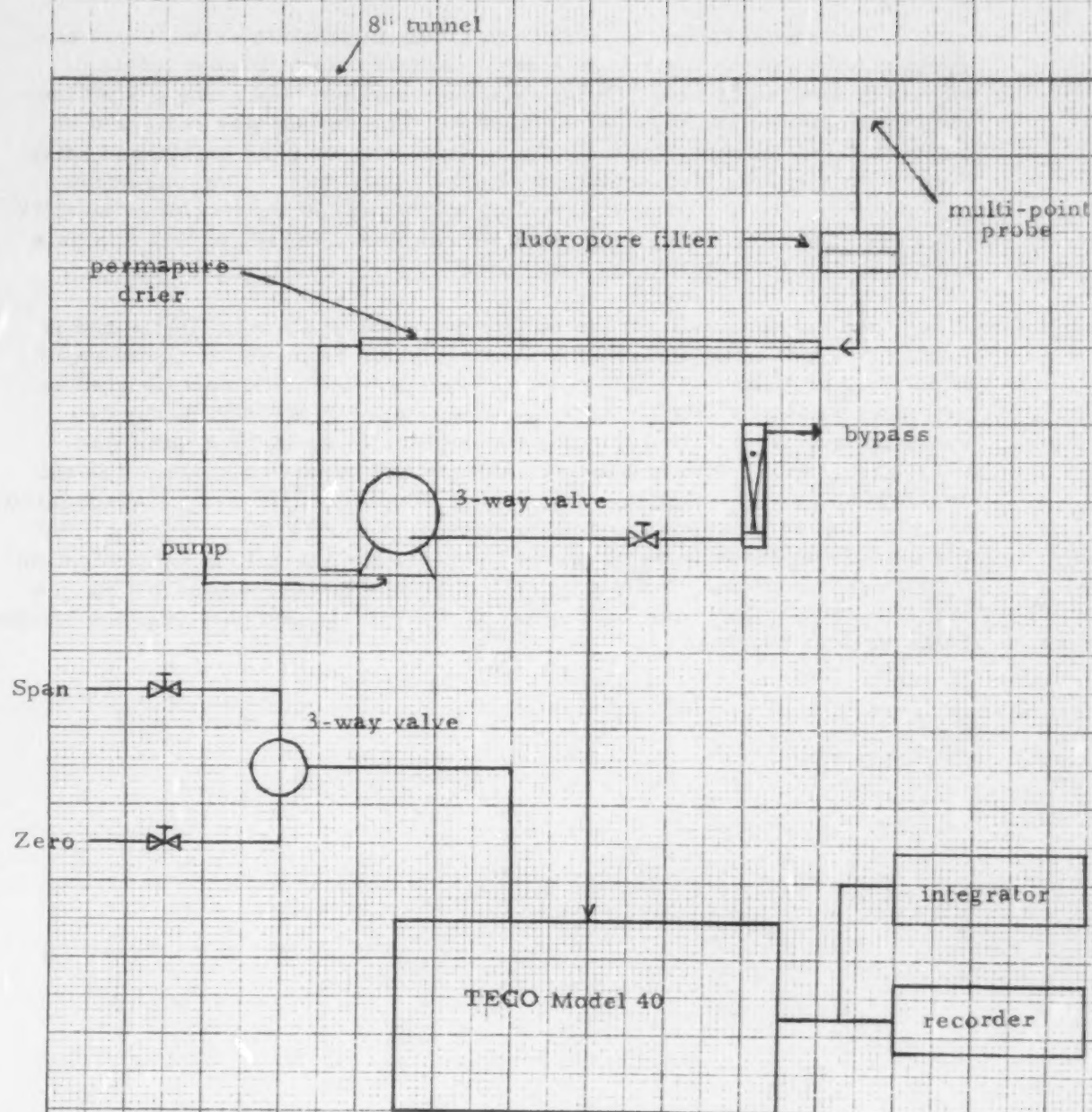


FIGURE A-3. TECO MODEL 40 SAMPLING INTERFACE
 FLOW SCHEMATIC

3. Sulfate (SO_4^{2-})

The measurement of sulfate in dilute automobile exhaust was accomplished by obtaining an iso-kinetic sample from a 10 foot length of an 8 inch dilution tunnel. These samples were obtained using a 3/8" iso-kinetic probe at a flow rate of 0.45 CFM. The sulfate was collected on a 47mm 0.5 μ fluoropore filter. Each filter was weighed before and after the test to allow the determination of particulate data. The extraction and analysis was performed according to the procedure developed by EPA⁽¹⁰⁾ (RTP) for the analysis of water soluble sulfates. A copy of this analysis is included in this section for reference.

A flow schematic of the sulfate sampling system is illustrated in Figure A-4 while the analytical instrumentation employed in the analysis of SO_4^{2-} is presented in Figure A-5. The specific instrument utilized in the measurement of SO_4^{2-} was a Beckman Model 25 UV-VIS Recording Spectrophotometer. An 18 μ l flow-through cell was incorporated into the system, along with necessary columns and pumps as specified in the analysis of soluble sulfates. Figure A-6 illustrates the barium chloranilate system used to measure the sulfate emissions during this program. Sulfuric acid standards were prepared to determine the sulfate concentrations in the filter extracts. Sulfate emission rates were calculated based on a single filter per test; and consequently, the sulfate and particulate emission rates are not weighted.

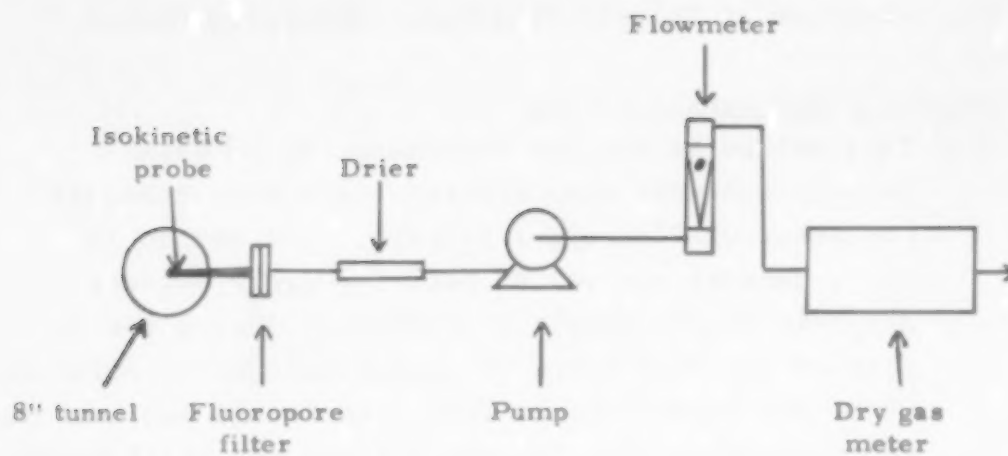


FIGURE A-4. SULFATE SAMPLING SCHEMATIC



FIGURE A-5. SULFATE SAMPLING SYSTEM

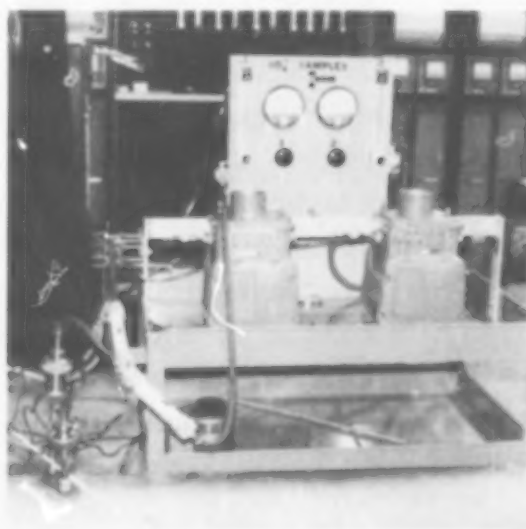


FIGURE A-6. BCA SO_4^{2-} SYSTEM

Determination of Soluble Sulfates: Automated Method

1. Principle and Applicability

- 1.1 This method is for the determination of water-soluble sulfates from diluted automobile exhausts collected on Fluoropore filters. The method is quite general and may be used for trace sulfate analysis of any sample from which sulfates can be leached out with water or aqueous alcoholic solutions. There are interferences from some anions and methods for minimizing or eliminating these are still being worked out. The method as written is applicable to sulfate analysis of exhaust emissions from cars run on non-leaded gasoline.
- 1.2 Auto exhaust is mixed with air in a dilution tunnel and sampled through isokinetic probes. SO_3 reacts with available moisture in the exhaust to form H_2SO_4 aerosols and is trapped on Fluoropore* filters with 0.45 μ pore size. The filter is extracted with 60/40 isopropyl alcohol/water solution (i.e. 60 ml isopropyl alcohol (IPA) + 40 ml water). The extract is fed by a high pressure liquid (chromatographic) pump through a column of cation exchange resin to remove cationic interferences and then through a column of solid barium chloranilate where BaSO_4 precipitates out. An equivalent amount of reddish colored acid chloranilate ion is released^{1,2} and is measured colorimetrically at 310 $\text{m}\mu$ ^{3,4}. To use this method for aqueous sulfate solutions, four parts by volume of the solution are mixed with six parts of IPA before feeding through the columns. Manual method or a dynamic sampling system can be used.

*Registered trade mark. Obtainable from Millipore Corp.

2. Range and Sensitivity

Working concentration range and sensitivity depend on sample size. A sensitivity better than $0.5 \mu\text{g SO}_4^{=}$ per ml in 60% IPA and working range of 0 - 25 $\mu\text{g/ml}$ were obtained using a 0.5 ml external sampling loop injection system in conjunction with a du Pont liquid chromatograph UV detector. Sensitivity may be further increased by increasing the alcohol content of the solvent, as this would further decrease the solubility of BaSO_4 and barium chloranilate. This, however, requires a much tighter control of the water/IPA ratio in the sample and in the mobile phase. To minimize spurious results arising from water imbalance, it is recommended that both the extracting solvent and the mobile phase for analytical runs be taken from the same stock solution. Sample size as large as 1.5 ml has been successfully used.

3. Interferences

Cations interfere negatively by reacting with the acid chloranilate to form insoluble salts. These, however, are conveniently removed by passing the sample through a cation exchange resin in the acid form. Some anions such as Cl^- , Br^- , F^- , $\text{PO}_4^{=}$ interfere positively by precipitating out as barium salts with subsequent release of acid chloranilate ions. Some buffer systems²⁻⁵ are reported to minimize anion interference. These systems are being investigated for possible incorporation in the present procedure. Alternative clean-up methods are also under consideration. Fortunately, for non-leaded exhaust samples collected on filters, ionic interference is minimal. Interference from aromatic compounds is minimized by using a 300 m μ cut-off filter in the optical path of the detector system.

4. Precision, Accuracy, and Stability

4.1 Precision

With an external sampling loop of about 1.5 ml, photometer attenuation set to read .04 absorbance units full scale, standard deviation of 0.05 $\mu\text{g SO}_4^{=}/\text{ml}$ was obtained for a sample containing 4.0 $\mu\text{g SO}_4^{=}/\text{ml}$.

4.2 Stability

4.2.1 Sulfuric acid standards containing 10 and 100 $\mu\text{g SO}_4^{=}/\text{ml}$ in 60% IPA are stable for at least one month when stored in tightly capped volumetric flask which has been cleaned with 1:1 nitric acid and copiously rinsed with deionized water. Alternative storage containers are capped polyethylene reagent bottles.

4.2.2 The cation exchange resin and the barium chloranilate columns as described in apparatus section last for over two months. For samples known to contain cations, it is advisable to remove these cations by external treatment with cation exchange resin prior to injection into the sampling loop.

4.2.3 As the barium chloranilate column is depleted each time sulfate samples are fed through, it is good practice to run sulfuric acid standards before and after the sample.

4.2.4 Exposure of alcoholic samples, standards, and solvents to the atmosphere should be minimized, since IPA solution picks up atmospheric water on standing.

5. Apparatus

A schematic of the principal components of the automated set-up is shown in Figure 1.

5.1 Hardware

- a. Reservoir (LR) for the solvent (60% IPA).
- b. High pressure liquid pump (LP) capable of delivering liquids at flow rates of up to 3 ml/min at pressures as high as 1000 psi. Most liquid pumps used in high pressure liquid chromatography would be satisfactory.
- c. Flow or pressure controller (FC).
- d. Six-port high pressure switching valve (SV) equipped with interchangeable external loop (L).
- e. Ultraviolet detector (D) equipped with appropriate filters to isolate a narrow band of radiation centered at 310 mμ. A microscope cover glass was found to be satisfactory.
- f. Recorder to monitor detector response.
- g. Automatic sampler (AS), such as the one used for a Technicon AutoAnalyzer.
- h. Peristaltic pump (PP) to draw sample into sampling loop.
- i. Cation exchange resin column (CX) - standard 1/4" O. D. x 10" stainless steel column packed with analytical grade Dowex 50W-X2 cation exchange resin in hydrogen form.
- j. Barium chloranilate column (BC) - standard 1/4" O. D. x 5" stainless steel column packed with barium chloranilate.

5.2 Principle of Operation

Solvent (60% IPA) in reservoir (LR) is continuously fed through cation exchange (CX) and barium chloranilate columns at flow rates of about 3 ml/min. by a high pressure liquid pump (LP). Background absorbance is continuously measured by a UV detector (D) at 310 m μ and visually monitored in a strip chart recorder. A solenoid actuated air operated switching valve (SV) is used for filling the external sampling loop (L) with samples in conjunction with an automatic sampler (AS) and peristaltic pump (PP) and injecting the sample into the columns. At CX cations are removed and at BC, color reaction takes place. The BaSO₄ precipitate is retained in the column while the acid chloranilate is carried by the solvent through the detector system for colorimetric measurement.

For an automated sampling system such as shown in Figure 1, both SV and PP are electrically coupled to AS by electric relays such that both are activated whenever AS is sampling (i.e. L is being filled and mobile phase bypasses L). At the end of the sampling cycle, PP and AS stop and SV switches to the injection mode (i.e. mobile phase passes through L and carries sample through CX and BC columns).

For manual operation SV may be retained or replaced by a similar switching valve equipped with an extended handle for manual switching. Samples may be introduced into the sampling loop by syringe injection or by peristaltic pump system similar to the one used in the automated system.

6. Reagents

- 6.1 Isopropyl alcohol (IPA) spectroquality grade or equivalent. Volatile solvent, safety class 1B.
- 6.2 60% IPA. Add four parts water to six parts IPA by volume. Store in tightly capped bottle. About three liters are needed for a 12 hour operation.
- 6.3 Barium chloranilate, suitable for sulfate analysis.
- 6.4 Dowex 50W-X2 cation exchange resin, hydrogen form, 100-200 mesh.
- 6.5 Hydrochloric acid (4N). Add 30 ml concentrated hydrochloric acid to 60 ml deionized water. (Danger, strong acid.)
- 6.6 Standard sulfuric acid (1N). Dilute to the mark 2.8 ml of concentrated sulfuric acid with deionized distilled water in a liter volumetric flask which has been washed in 1:1 nitric acid and copiously rinsed with deionized distilled water. Standardized against accurately weighed sodium carbonate to get exact normality. 0.1N H_2SO_4 is equivalent to 4800 $\mu\text{g}/\text{SO}_4=\text{ml}$. (Danger, strong acid.)
- 6.7 Standard sulfate solution (1000 $\mu\text{g SO}_4=\text{ml}$). Dissolve 1.4787 gm sodium sulfate which has been heated up to 105°C for four hours and cooled in a dessicator and dilute to 1000 ml.

7. Procedure

7.1 Column preparation

- 7.1.1 Barium chloranilate column (BC). In order to prepare a full column with minimum dead volume connect two lengths of standard 1/4" O. D. stainless steel tubings as shown in Figure 2. $b = 2"$, $a = 5"$. Connect a small funnel to open end of B with a Tygon tubing sleeve.

Fill the funnel half way with barium chloranilate and use a vibrator (i.e. electric pencil engraver) to pack the solid in column. Continue operation until B is about half filled.  Remove funnel, plug empty space with glass wool, and cap the end with a 1/4" to 1/16" reducer. Plumb column B directly to SV in Figure 1. Connect a Tygon tubing at A and direct tubing to waste reservoir. Activate liquid pump, set flow controller at pressure drop of about 600 psi. Let solvent flow for 20 minutes. Deactivate pump, disconnect column from SV. Disconnect column A from column B. Connect a glass wool-plugged 1/4" to 1/16" reducer to uncapped end of column A.

- 7.1.2 Cation exchange resin column (CX). Add cation exchange resin, 100-200 mesh, Dowex 50W-X2 to 80 ml of 4N HCl in a 150 ml beaker until a wet volume equivalent to 20 ml has settled at the bottom. Let soak for at least three hours with occasional stirring using a glass rod. Decant the acid, add 100 ml deionized distilled water, stir and slowly decant the liquid as soon as most of the solid has settled down at the bottom. Repeat rinsing procedure several times until rinse liquid gives a neutral reaction to pH paper.

Connect two standard 1/4" O. D. stainless steel tubings as in 7.1.1 with $b = 5"$ and $a = 10"$. Connect a small funnel to open end of B with Teflon or Tygon tubing sleeve. Clamp composite tube vertically and connect

open end of A to vacuum line equipped with liquid trap. Fill funnel with deionized distilled water and turn on vacuum slowly until composite tube is completely filled with water. Add water until funnel is half-filled, stop vacuum and add slurry of freshly washed resin. Let resin settle by gravity until resin top is seen above B. Turn on vacuum slowly, keep adding resin slurry until composite tube is completely filled. Proceed as in 7.1.1 beginning with sentence: "Remove funnel, plug empty space..."

7.2 Priming System for Analytical Run

Connect the cation exchange and barium chloranilate columns with 1/4" union packed with glass wool as shown in Figure 1. Fill solvent reservoir (LR) with 60% IPA, activate liquid pump, detector, recorder, switching valve, sampler, and peristaltic pump. Allow to cycle normally to clean out all components. For this initial operation, dip the sampling probe in at least 100 ml of 60% IPA. Set liquid flow rate at about 3 ml/min. Let run for at least 30 minutes. Deactivate switching valve, sampler, and peristaltic pump. Leave other components in operating mode. When background is stable at attenuation of .01 absorbance units full scale, system is ready for analysis.

7.3 Preparation of Calibration Standards

Either sulfuric acid or sodium sulfate standards may be used.

Add 200 ml of 0.1 N H_2SO_4 aqueous stock solution to 300 ml 100% IPA in 500 ml volumetric flask. (Note: There is a volume decrease of about 2.7% when these

proportions of water and IPA are mixed.) Dilute to the mark with 60% IPA. This is equivalent to $1,920 \mu\text{g SO}_4^-/\text{ml}$ in 60% IPA. Prepare from this alcoholic stock solution calibration standards in the range $0.5 - 25 \mu\text{g SO}_4^-/\text{ml}$ by dilution of appropriate aliquots with 60% IPA.

- 7.4 Extraction of Soluble Sulfates from Fluoropore Filters
Place filter in one oz. polyethylene bottle, add 10 ml 60% IPA and cap tightly. Shake until filter collapses and is completely immersed in liquid. Let stand overnight.

7.5 Analysis

Set instrument in operating mode, remove sampling probe from holder, and dip in 100 ml 60% IPA. Let it run at flow rate of 3 ml/min until stable background is obtained, then remount sampling probe to holder. In the meantime, fill sample cuvettes with sample extract and blank solutions (60% IPA) and place on turntable. Sampling pattern is blank, blank, sample, blank, blank at the rate of about six minutes per sample or blank. Blanks are used to wash out system between samples and minimize sample overlap. One blank between samples is adequate for dilute samples. (See also 5.2.)

A series of standards (see 7.3) is run, preferably before sample runs and calibration curve, peak height vs. concentration, is plotted. A control standard may also be placed after every ten samples as a quality check on the stability of the system.

The plot of peak height (detector response) vs. concentration ($\mu\text{g SO}_4^-/\text{ml}$) is non-linear in the low concentration end as would be expected from solubilities and kinetics consideration. Non-linearity is also observed at the upper end of the curve.

8. Calculations

Calculate the concentration of sulfate as $\mu\text{g SO}_4 = / \text{ml}$ using the calibration curve. Total soluble sulfates

$[\text{SO}_4]_F$ in filter is then given by:

$$[\text{SO}_4]_F = (\mu\text{g SO}_4 = / \text{ml}) \times V_o \times d$$

where: V_o = total volume of original sample extract

d = dilution factor

Example: Suppose 10 ml 60% IPA was used to extract the soluble sulfates in the filter and that 2 ml of this was diluted further to 6 ml with 60% IPA to bring detector response within calibration range. Suppose that the concentration of the diluted sample was found to be 5 $\mu\text{g/ml}$. Then,

$$[\text{SO}_4]_F = (5 \mu\text{g/ml}) \times 10 \text{ ml} \times \frac{6}{2} = 150 \mu\text{g}.$$

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FIGURE 1
FLOW SCHEMATIC FOR AUTOMATED SULFATE INSTRUMENT

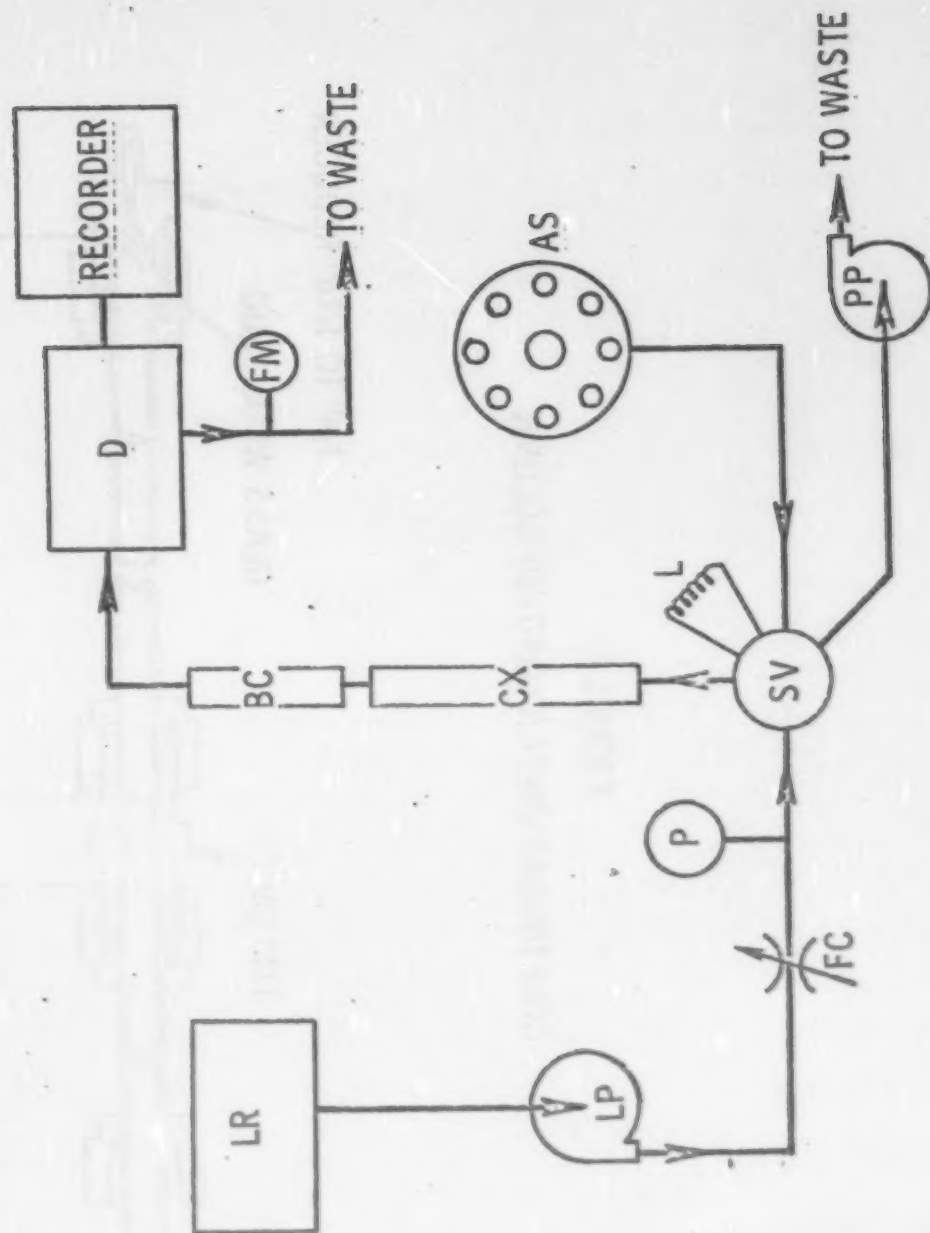
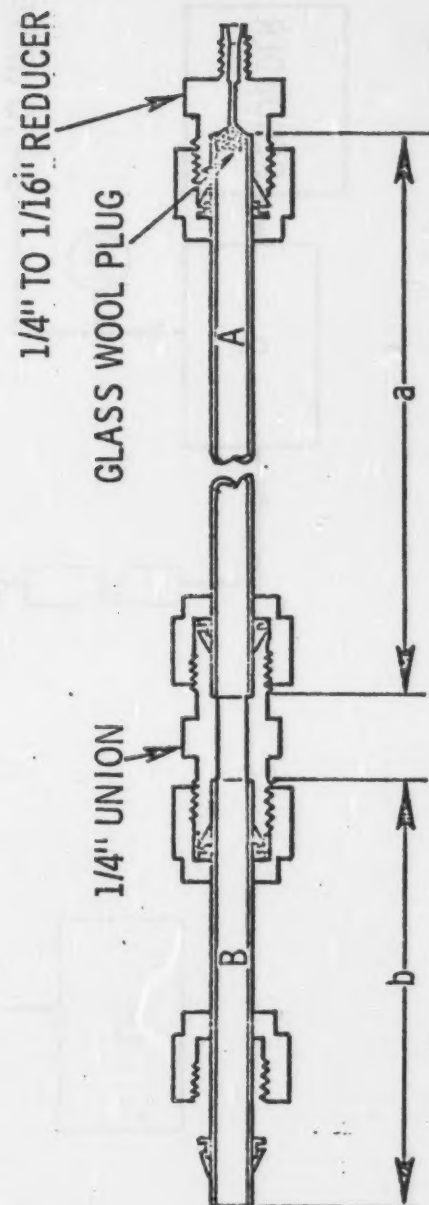


FIGURE 2
CONFIGURATION FOR LOADING COLUMN



Barium Chloranilate Interference Experiments - During the course of the project, several fuel and fuel additive combinations will be used, all of which will require sulfate analysis using the barium chloranilate procedure. Although a cation exchange column is included as part of the sampling system, concern has been expressed for the analysis of sulfate on engines operating on leaded fuel. The Dowex 50W X-2 cation exchange column has been included to eliminate or at least reduce any lead that might be collected on the filters for sulfate analysis. Since the efficiency of the cation exchange column may not remove all of the lead ions, it was decided to conduct a series of experiments to determine how much interference from lead might be expected. These experiments were conducted with an ion exchange column, which had been used for about one month on lead free samples.

A working sulfate standard of $23.93 \mu\text{g SO}_4^{=}/\text{ml}$ was used to make comparisons with the various lead blends. Lead nitrate blends were prepared in 60 percent IPA in concentrations of 25.0, 12.5, and $5.0 \mu\text{g Pb}^{++}/\text{ml}$. These solutions were analyzed in the same manner as an extracted sample, and the corresponding peak was calculated as response as $\mu\text{g SO}_4^{=}/\text{ml}$. These data is presented in Table A-1 and shown graphically in Figure A-7. The response as $\mu\text{g SO}_4^{=}/\text{ml}$ varied from 2.7 to $0.7 \mu\text{g SO}_4^{=}/\text{ml}$ with Pb^{++} concentrations ranging from 25 to $5 \mu\text{g Pb}^{++}/\text{ml}$. It was apparent that not all of the lead is being removed by the ion exchange column.

Since lead is generally added to the fuel in the form of a motor mix containing ethylene dichloride and ethylene dibromide as scavengers, it was decided to determine if these could produce erroneous results. The first experiment involved the preparation of three concentrations of chloride in 60 percent IPA. Sodium chloride was used in the preparation of the 24.3, 12.1, and $4.8 \mu\text{g Cl}^{-}/\text{ml}$. Again, these blends were analyzed just as a normal sulfate sample and the corresponding peak calculated as response as $\mu\text{g}/\text{SO}_4^{=}/\text{ml}$. These results are found in Table A-1, and $\mu\text{g Cl}^{-}/\text{ml}$ as a function of response as $\mu\text{g SO}_4^{=}/\text{ml}$ is shown in Figure A-7. The response as $\mu\text{g SO}_4^{=}/\text{ml}$ varied from 7.1 to 2.1 with a range in $\mu\text{g Cl}^{-}/\text{ml}$ of 24.3 to 5.0. In comparison with the experiment in lead interference, it was found that the chloride ions produced some three to four times greater interference than the lead ions alone.

A similar experiment involving the interference of bromide ions was conducted. Sodium bromide was added to 60 percent IPA in concentrations 31.1, 15.5, and $6.2 \mu\text{g Br}^{-}/\text{ml}$. These blends were also analyzed according to the standard barium chloranilate procedure. The range of response as $\mu\text{g SO}_4^{=}/\text{ml}$ was from 5.1 to 1.9 for the concentrations of Br^{-} tested.

Of the three interference species evaluated, it appears that with the normal barium chloranilate procedure lead has the least interference

TABLE A-1. EFFECT OF LEAD CHLORIDE AND BROMIDE IONS
ON SULFATE RESULTS USING THE BARIUM CHLORANILATE
LIQUID CHROMATOGRAPH PROCEDURE

<u>Sample Description</u>	<u>Response as $\mu\text{g SO}_4^{=}/\text{ml}$</u>	<u>$\mu\text{g Pb}^{++}/\text{ml}:\mu\text{g SO}_4^{=}/\text{ml}$</u>
23.93 $\mu\text{g SO}_4^{=}/\text{ml}$	23.93	
25.0 $\mu\text{g Pb}^{++}/\text{ml}$	1.71	14.6
12.5 $\mu\text{g Pb}^{++}/\text{ml}$	0.66	18.9
5.0 $\mu\text{g Pb}^{++}/\text{ml}$	0.33	15.1
		<u>$\mu\text{g Cl}^{-}/\text{ml}:\mu\text{g SO}_4^{=}/\text{ml}$</u>
24.3 $\mu\text{g Cl}^{-}/\text{ml}$	7.06	3.4
12.1 $\mu\text{g Cl}^{-}/\text{ml}$	4.23	2.9
4.8 $\mu\text{g Cl}^{-}/\text{ml}$	2.12	2.3
		<u>$\mu\text{g Br}^{-}/\text{ml}:\mu\text{g SO}_4^{=}/\text{ml}$</u>
31.1 $\mu\text{g Br}^{-}/\text{ml}$	5.07	6.1
15.5 $\mu\text{g Br}^{-}/\text{ml}$	4.04	3.8
6.2 $\mu\text{g Br}^{-}/\text{ml}$	1.92	3.2

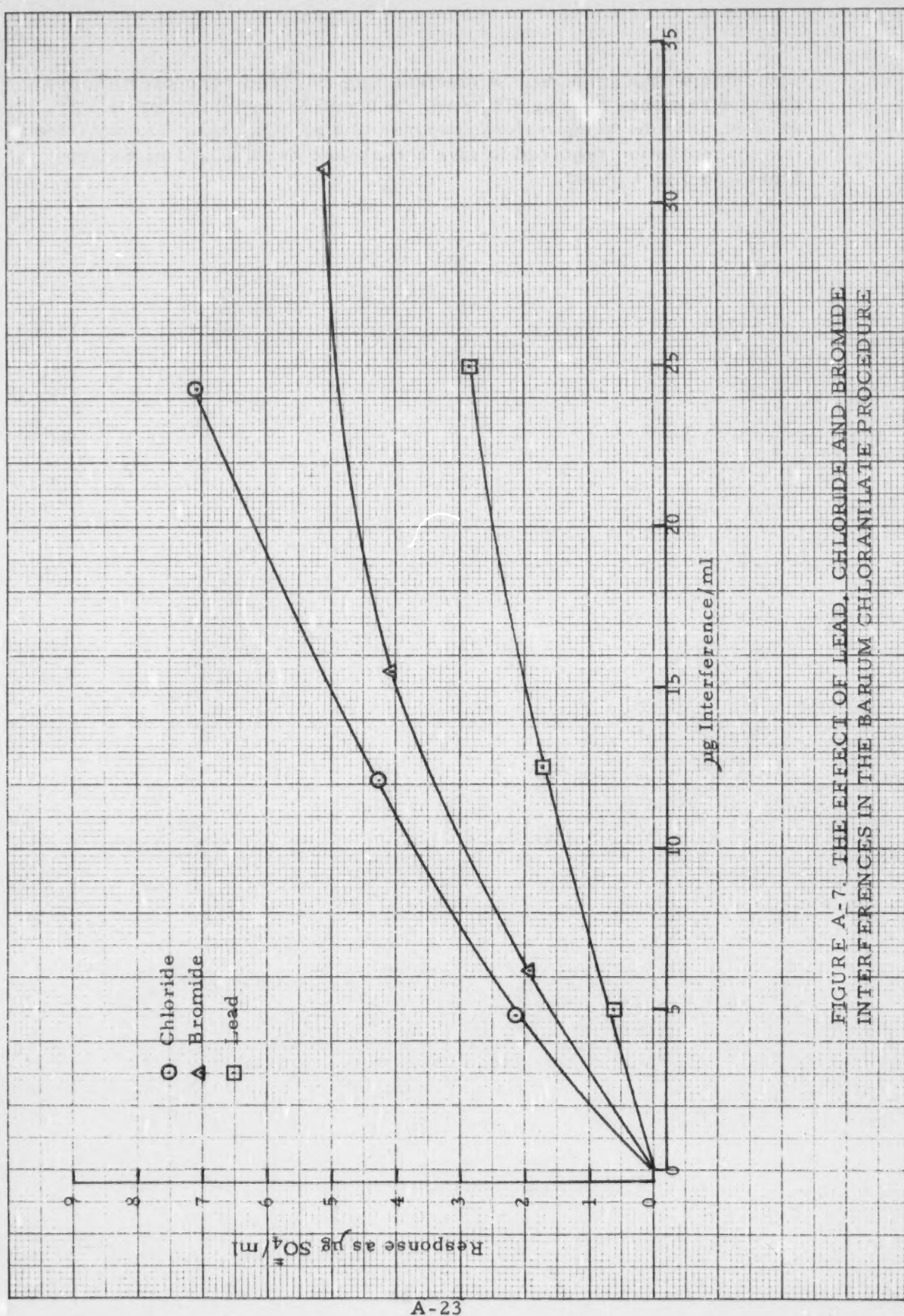


FIGURE A-7. THE EFFECT OF LEAD, CHLORIDE AND BROMIDE INTERFERENCES IN THE BARIUM CHLORANILATE PROCEDURE

and chloride the greatest. A nominal $7\text{ }\mu\text{g Pb}^{++}/\text{ml}$ concentration produced a response as $1\text{ }\mu\text{g SO}_4^{=}/\text{ml}$. A bromide concentration of $3\text{ }\mu\text{g Br}^{-}/\text{ml}$ provide an equivalent response to $1\text{ }\mu\text{g SO}_4^{=}/\text{ml}$. The chloride ion concentration required to give a response as $\mu\text{g SO}_4^{=}/\text{ml}$ ranged from 2 to $3\text{ }\mu\text{g Cl}^{-}/\text{ml}$.

4. Nitrogen Compounds

The nitrogen compounds included in this analysis were nitromethane (CH_3NO_2), dimethylnitrosamine (DMNA), and ammonia (NH_3). This analysis was conducted using two different analytical systems. A gas chromatograph equipped with a Hall Electrolytic Conductivity detector was used for each analysis. The major difference was column arrangement in that the DMNA and CH_3NO_2 used a 3' x 1/4" glass column packed with Chromosorb 101. The furnace was maintained at 600°C with the detector in the reductive mode. A helium carrier gas flow rate of 80 ml/min was used, and the column was programmed from 100°C to 165°C at 7.5°C/min. Dilute liquid calibration standards were prepared and comparisons were made to the samples. Individual bag samples were analyzed for DMNA and CH_3NO_2 using a 5 ml gas tight syringe. A summary of the gas chromatograph operating conditions for the analysis of CH_3NO_2 and DMNA are presented in Table A-2.

The analysis for ammonia in the dilute exhaust bag samples was conducted using a Hall Electrolytic Conductivity detector without the furnace, connected directly to the detector. A 3' x 1/4" Teflon column packed with 20 to 30 mesh Ascarite was used to remove any acid gases. A helium carrier gas was used at a flow rate of 150 ml/min and was operated isothermally at room temperature. Calibration standards were prepared and used for direct comparison to the dilute exhaust samples. Sample injections of both standards and samples were made using a 1 ml gas tight syringe. A summary of the gas chromatograph operating conditions is presented in Table A-2. Figure A-8 illustrates the gas chromatograph system used in the analysis of the nitrogen compounds.

TABLE A-2. SUMMARY OF GAS CHROMATOGRAPH
OPERATING CONDITIONS USED IN THE ANALYSIS OF
SULFUR AND NITROGEN COMPOUNDS

Parameter	H ₂ S, COS, Mercaptans	CH ₃ NO ₂ , DMNA	Ammonia
Instrument	Tracor MT 220	Tracor MT 200	Tracor MT 200
Column	12' x 1/8" teflon	3' x 1/4" glass	3' x 1/4" teflon
Column Packing	Chromosorb 102	Chromosorb 101	20-30 mesh Ascarite
Carrier gas	N ₂	He	He
Carrier flow	60 ml/min	80 ml/min	150 ml/min
Column temp	room	100-165 @ 7.5°C/min	room
Detector	Flame photometric (S-mode)	Hall ECD @ 600°C (Reductive mode)	Hall ECD (no furnace)
Sample size	10 ml sample loop	5 ml glass syringe	1 ml syringe
Minimum detection limits	50 ppb H ₂ S 25 ppb COS 100 ppb CH ₃ SH 300 ppb C ₂ H ₅ SH	0.04 ppm CH ₃ NO ₂ 0.06 ppm DMNA	0.5 ppm NH ₃

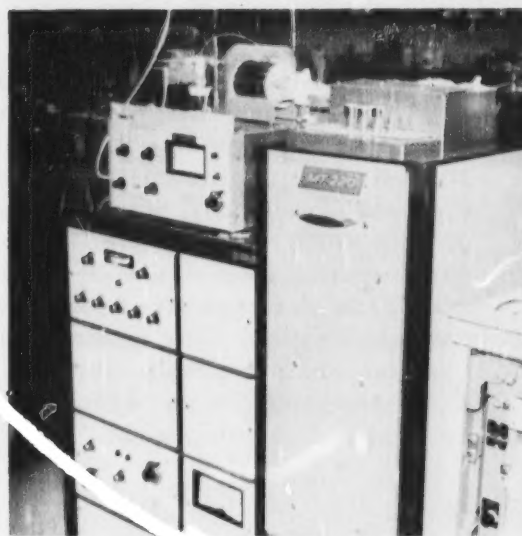
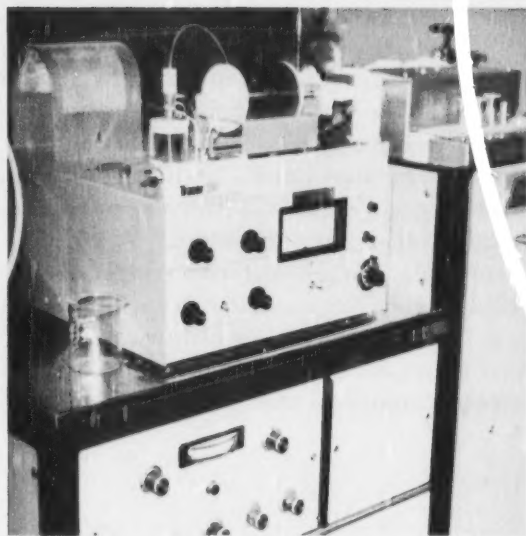


FIGURE A-8. GAS CHROMATOGRAPH SYSTEM USED FOR ANALYSIS OF NITROMETHANE, DIMETHYLNITROSAMINE AND AMMONIA

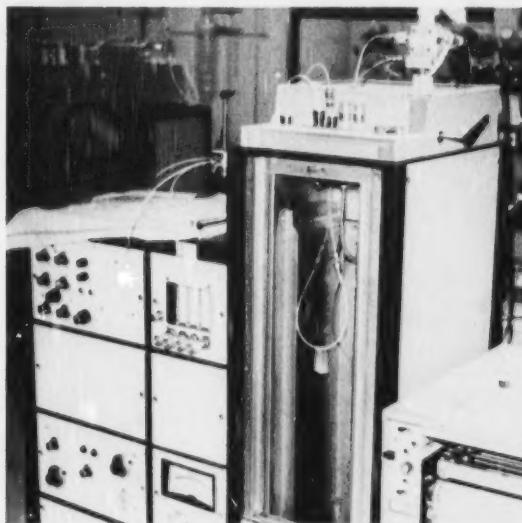


FIGURE A-9. GAS CHROMATOGRAPH SYSTEM USED FOR ANALYSIS OF HYDROGEN SULFIDE, CARBONYL SULFIDE, METHYL AND ETHYL MERCAPTAN

5. Sulfur Compounds

The measurement of sulfur compounds was conducted using a Tracor MT 220 gas chromatograph equipped with a flame photometric detector operating in the S mode. A 12" x 1/8" Teflon column packed with Chromosorb 102 operating isothermally at room temperature was used. A nitrogen carrier gas flow rate of 60 ml/min was found to give a satisfactory separation of H_2S , COS , CH_3SH , and $\text{C}_2\text{H}_3\text{SH}$ in dilute automotive exhaust. A 10 ml gas sampling loop was used for sample and calibration standard injections. Standards were prepared for the individual sulfur compounds on a daily basis as needed. The minimum detection limits as well as a summary of the gas chromatograph operating conditions are found in Table A-2. Figure A-9 illustrates the gas chromatograph system used in the analysis of the various sulfur compounds.

INDIVIDUAL HYDROCARBON DISTRIBUTION

INDIVIDUAL HYDROCARBON DISTRIBUTION

TABLE B-1. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND
SEVERAL REACTIVE HYDROCARBONS MEASURED DURING
1975 LD FTP ON 1972 350 CID CHEVROLET ENGINE
(EM-214-F, Base Fuel at 0.1% Sulfur)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
12-16-74 (0 Miles)	1	1	13.7	2.1	14.4	0.0	3.3	20.7	9.5	32.8
		2	9.5	1.2	10.2	0.0	2.5	14.8	6.0	15.8
		3	10.8	1.8	13.1	0.0	3.1	21.4	8.9	28.4
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-16-74 (0 Miles)	2	1	10.5	1.8	12.7	0.0	3.2	20.9	12.7	31.9
		2	10.0	1.0	8.2	0.0	2.1	11.5	4.9	11.6
		3	9.6	1.6	11.6	0.0	2.3	19.1	7.9	23.9
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-23-74 (1000 Miles)	1	1	13.9	1.6	13.1	0.0	2.7	19.9	8.3	21.8
		2	10.2	1.0	11.1	0.0	1.6	13.1	4.9	12.2
		3	12.2	1.7	14.4	0.0	3.2	20.6	8.2	23.8
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-23-74 (1000 Miles)	2	1	11.6	1.7	13.4	0.0	3.0	20.2	8.4	22.7
		2	8.8	0.9	9.3	0.0	2.6	11.9	4.5	10.2
		3	9.8	1.5	11.7	0.0	2.4	17.9	7.4	23.0
		BG	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-31-74 (2000 Miles)	1	1	11.2	1.5	13.2	0.0	8.2	17.8	7.2	15.5
		2	10.5	1.0	10.3	0.0	9.2	12.2	4.6	9.3
		3	12.4	1.3	11.8	0.0	8.3	16.5	6.7	17.8
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-31-74 (2000 Miles)	2	1	11.6	1.5	13.3	0.0	9.0	17.6	7.0	19.2
		2	11.4	0.9	10.0	0.0	6.6	11.5	4.2	8.7
		3	13.1	1.4	12.9	0.0	7.9	17.1	6.8	17.5
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B-2. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND SEVERAL REACTIVE HYDROCARBONS MEASURED DURING 1975 LD FTP ON 1972 350 CID CHEVROLET ENGINE (EM-215-F at 0.1% Sulfur + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	NRHC Concentration, ppm C					Reactive HC's Measured, ppm C		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
2-10-75 (0 Miles)	1	1	7.9	1.2	9.0	0.0	2.7	12.4	5.1	15.1
		2	6.6	0.7	6.6	0.0	2.1	8.5	3.4	7.3
		3	7.8	1.1	9.0	0.0	2.7	13.0	5.6	16.9
		BG	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-10-75 (0 Miles)	2	1	6.4	0.9	7.4	0.0	2.2	11.6	4.8	12.0
		2	5.6	0.6	5.7	0.0	1.7	7.6	2.9	5.2
		3	7.0	1.0	8.1	0.0	2.6	12.2	5.2	14.1
		BG	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-13-75 (1000 Miles)	1	1	6.9	0.8	6.7	0.0	2.0	11.1	4.7	11.2
		2	6.7	0.5	5.0	0.0	1.5	6.9	2.7	4.8
		3	6.8	0.8	6.6	0.0	2.0	10.6	4.4	10.7
		BG	3.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-13-75 (1000 Miles)	2	1	6.2	0.8	6.9	0.0	2.1	10.7	4.5	11.2
		2	5.4	0.5	5.2	0.0	1.6	5.8	2.6	4.4
		3	6.0	0.8	6.5	0.0	2.2	10.0	4.1	10.7
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-18-75 (2000 Miles)	1	1	7.2	0.8	8.3	0.0	2.5	11.6	4.7	10.7
		2	6.1	0.5	6.2	0.0	1.9	7.3	2.8	5.2
		3	6.3	0.8	7.1	0.0	2.4	10.8	4.6	11.5
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-18-75 (2000 Miles)	2	1	6.8	0.8	7.4	0.0	2.3	11.1	4.5	10.5
		2	5.2	0.5	4.9	0.1	1.4	6.5	2.5	4.4
		3	6.2	0.7	6.9	0.0	1.9	10.3	4.2	10.0
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B-3. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND
SEVERAL REACTIVE HYDROCARBONS MEASURED DURING
1975 LD FTP ON 1972 350 CID CHEVROLET ENGINE
(EM-216-F at 0.1% Sulfur + 0.486 g/gal Paradyne 506)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
1-10-75 (0 Miles)	1	1	12.7	1.6	16.0	0.0	3.9	19.3	7.9	22.1
		2	10.1	1.0	11.8	0.0	2.3	13.1	4.7	10.5
		3	12.9	1.5	15.0	0.0	3.8	19.2	7.8	25.9
		BG	3.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-10-75 (0 Miles)	2	1	11.4	1.6	14.3	0.0	4.3	18.5	7.5	22.7
		2	8.9	0.9	10.3	0.0	3.0	12.2	4.4	8.9
		3	10.3	1.3	12.5	0.0	2.9	16.8	6.8	19.7
		BG	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-13-75 (1000 Miles)	1	1	6.8	0.9	7.8	0.0	1.5	11.9	4.9	14.5
		2	5.2	0.4	5.1	0.0	1.4	6.7	2.4	4.3
		3	7.1	0.8	7.1	0.0	1.4	10.5	4.2	12.2
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-13-75 (1000 Miles)	2	1	7.2	0.8	8.3	0.0	1.5	12.3	5.0	14.8
		2	4.8	0.4	4.5	0.0	1.2	6.9	2.5	4.9
		3	5.5	0.7	6.1	0.6	1.5	10.1	4.0	11.4
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-20-75 (2000 Miles)	1	1	8.0	0.8	8.1	0.0	1.8	12.3	5.0	10.6
		2	9.1	0.5	5.4	0.0	1.5	7.0	2.7	4.4
		3	7.6	0.8	8.5	0.0	1.9	11.6	4.7	10.3
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-20-75 (2000 Miles)	2	1	7.3	0.8	8.6	0.0	1.7	11.7	4.6	11.9
		2	5.6	0.4	5.3	0.0	1.2	7.0	2.6	4.1
		3	6.2	0.7	6.7	0.0	1.3	10.6	4.2	10.1
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B-4. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND SEVERAL REACTIVE HYDROCARBONS MEASURED DURING 1975 LD FTP ON 1972 350 CID CHEVROLET ENGINE (EM-231-F at 0.1% Sulfur + 0.378 g/gal Lubrizol 8101 + 0.05g Pb/gal)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
3-11-75 (0 Miles)	1	1	8.6	1.1	9.6	0.0	3.4	13.8	5.5	16.6
		2	7.2	0.7	7.1	0.0	2.5	8.6	3.3	7.7
		3	8.4	1.1	9.2	0.0	3.2	12.6	5.2	15.0
		BG	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-11-75 (0 Miles)	2	1	8.3	1.1	9.2	0.0	3.4	12.7	5.3	16.2
		2	7.4	0.7	7.6	0.0	2.8	9.0	3.5	7.1
		3	8.3	1.1	9.4	0.0	3.4	12.6	5.2	14.7
		BG	1.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-14-75 (1000 Miles)	1	1	8.2	0.9	9.3	0.0	2.9	12.1	4.9	13.6
		2	6.5	0.5	6.3	0.0	2.1	7.1	2.6	5.8
		3	8.2	0.9	8.8	0.0	2.8	11.5	4.6	13.4
		BG	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-14-75 (1000 Miles)	2	1	7.4	0.9	8.2	0.0	2.7	11.3	4.5	12.3
		2	6.7	0.5	6.5	0.0	2.2	7.5	2.9	5.4
		3	8.0	0.9	8.5	0.0	2.7	11.6	4.6	12.7
		BG	2.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-21-75 (2000 Miles)	1	1	7.7	0.7	8.8	0.0	3.1	12.2	4.9	14.6
		2	7.3	0.6	7.2	0.0	2.6	8.4	3.1	6.6
		3	7.8	0.9	8.8	0.0	3.0	11.6	4.7	13.5
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-21-75 (2000 Miles)	2	1	9.2	1.0	10.6	0.0	3.3	13.2	5.6	15.6
		2	7.1	0.7	7.5	0.0	2.6	8.3	2.9	6.5
		3	8.3	1.0	9.3	0.0	3.1	11.8	4.8	13.3
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B-5. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND SEVERAL REACTIVE HYDROCARBONS MEASURED DURING 1975 LD FTP ON 1975 350 CID CHEVROLET ENGINE (EM-214-F, Base Fuel at 0.1% Sulfur)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
12-17-74 (0 Miles)	1	1	10.8	0.8	0.0	0.0	0.2	2.5	6.9	0.1
		2	8.1	0.0	0.0	0.0	0.0	0.0	3.2	0.0
		3	9.8	0.7	0.0	0.0	0.1	1.9	1.7	0.1
		BG	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-17-74 (0 Miles)	2	1	8.2	0.7	0.0	0.0	0.1	1.5	0.0	0.1
		2	6.4	0.1	0.0	0.0	0.0	0.0	0.0	0.0
		3	7.8	0.5	0.0	0.0	0.0	1.2	0.0	0.0
		BG	2.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-20-74 (1000 Miles)	1	1	10.4	0.6	0.0	0.0	0.0	1.9	0.0	0.0
		2	11.2	0.2	0.0	0.0	0.0	0.2	0.0	0.0
		3	11.2	0.6	0.0	0.0	0.0	2.1	0.0	0.0
		BG	5.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-20-74 (1000 Miles)	2	1	14.0	0.7	0.0	0.0	0.0	2.3	0.0	0.0
		2	12.5	0.2	0.0	0.0	0.0	0.3	0.0	0.0
		3	14.8	0.7	0.0	0.0	0.0	1.8	0.0	0.0
		BG	6.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-30-74 (2000 Miles)	1	1	14.8	1.1	1.1	0.0	tr	5.1	tr	0.1
		2	10.6	0.5	0.0	0.0	0.0	1.1	0.0	0.0
		3	13.7	1.0	1.0	0.0	tr	3.9	tr	tr
		BG	2.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12-30-74 (2000 Miles)	2	1	11.6	1.0	0.6	0.0	tr	5.1	tr	tr
		2	10.1	0.4	0.0	0.0	tr	1.0	0.0	0.0
		3	11.7	0.9	0.9	0.0	tr	4.2	tr	tr
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

tr = trace, less than 0.05 ppmC but greater than 0.01 ppmC

TABLE B-6. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND
SEVERAL REACTIVE HYDROCARBONS MEASURED DURING
1975 LD FTP ON 1975 350 CID CHEVROLET ENGINE
(EM-215-F at 0.1% Sulfur + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
2-7-75 (0 Miles)	1	1	8.6	0.5	0.0	0.0	0.5	2.0	0.2	0.0
		2	6.5	0.2	0.0	0.0	0.0	0.1	0.0	0.0
		3	7.9	0.5	0.1	0.0	0.0	1.7	0.0	0.4
		BG	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-7-75 (0 Miles)	2	1	8.4	0.5	0.0	0.0	0.0	1.8	0.0	0.0
		2	6.8	0.2	0.0	0.0	0.0	0.2	0.0	0.0
		3	8.3	0.4	0.0	0.0	0.0	1.9	0.0	0.0
		BG	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-14-75 (1000 Miles)	1	1	8.3	0.5	0.5	0.0	0.0	1.5	0.0	0.0
		2	6.7	0.1	0.2	0.0	0.0	0.0	0.0	0.0
		3	8.1	0.5	0.4	0.0	0.0	1.2	0.0	0.0
		BG	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-14-75 (1000 Miles)	2	1	7.2	0.4	0.2	0.0	0.0	1.3	0.0	0.0
		2	6.5	0.2	0.0	0.0	0.0	0.2	0.0	0.0
		3	7.6	0.4	0.4	0.0	0.4	1.6	0.1	0.0
		BG	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
21-7-75 (2000 Miles) Miles)	1	1	8.0	0.5	0.3	0.0	0.0	1.2	0.0	0.0
		2	6.6	0.2	0.0	0.0	0.0	0.1	0.0	0.0
		3	8.3	0.5	0.1	0.0	0.0	1.7	0.0	0.0
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-17-75 (2000 Miles)	2	1	7.8	0.5	0.1	0.0	0.0	1.7	0.0	0.0
		2	6.1	0.3	0.0	0.4	0.0	0.1	0.0	0.0
		3	7.1	0.4	0.1	0.0	0.0	1.1	0.0	0.0
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0

TABLE B-7. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND SEVERAL REACTIVE HYDROCARBONS MEASURED DURING 1975 LD FTP ON 1975 350 CID CHEVROLET ENGINE (EM-216-F at 0.1% Sulfur + 0.486 g/gal Paradyne 506)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
1-9-75 (0 Miles)	1	1	15.4	0.9	0.4	0.0	3.2	5.0	tr	3.6
		2	8.9	0.2	0.0	0.0	0.0	0.7	0.0	0.0
		3	14.2	0.7	0.3	0.0	tr	3.7	tr	tr
		BG	3.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-9-75 (0 Miles)	2	1	12.4	0.7	0.3	0.0	1.6	4.0	tr	2.3
		2	8.5	0.2	0.0	0.0	tr	0.6	0.0	0.0
		3	15.1	0.5	0.0	0.0	0.9	1.8	0.0	1.1
		BG	2.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-14-75 (1000 Miles)	1	1	10.6	0.5	0.2	0.0	3.0	2.5	tr	1.5
		2	6.3	0.1	0.0	0.0	0.0	0.3	tr	0.0
		3	11.9	0.6	0.0	0.0	2.6	2.9	tr	1.0
		BG	2.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-14-75 (1000 Miles)	2	1	9.4	0.6	0.0	0.0	2.6	2.8	tr	1.0
		2	9.4	0.2	0.0	0.0	1.6	0.4	0.0	0.0
		3	8.3	0.4	0.3	0.0	1.8	1.7	0.0	0.8
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-17-75 (2000 Miles)	1	1	9.9	0.5	tr	0.0	1.6	1.7	tr	0.8
		2	6.3	0.2	0.0	0.0	0.5	0.2	0.0	0.0
		3	7.9	0.4	0.0	0.0	0.9	1.4	0.0	0.6
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1-17-75 (2000 Miles)	2	1	10.1	0.6	0.2	0.0	1.6	3.0	0.0	0.9
		2	7.2	0.2	0.0	0.0	0.5	0.2	0.0	0.0
		3	9.0	0.5	0.0	0.0	1.5	1.9	0.0	0.7
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0

tr = trace, less than 0.05 ppmC but greater than 0.01 ppmC

TABLE B-8. HYDROCARBON DISTRIBUTION OF NON-REACTIVE AND
SEVERAL REACTIVE HYDROCARBONS MEASURED DURING
1975 LD FTP ON 1975 350 CID CHEVROLET ENGINE
(EM-218-F at 0.1% Sulfur + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	NRHC Concentration, ppmC					Reactive HC's Measured, ppmC		
			CH ₄	C ₂ H ₆	C ₂ H ₂	C ₃ H ₈	C ₆ H ₆	C ₂ H ₄	C ₃ H ₆	C ₇ H ₈
3-10-75 (0 Miles)	1	1	8.0	0.5	0.2	0.0	1.0	1.2	0.0	1.4
		2	5.9	0.3	0.0	0.0	0.0	0.1	0.0	0.0
		3	7.0	0.5	0.0	0.0	0.0	1.1	0.0	1.0
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-10-75 (0 Miles)	2	1	7.4	0.5	0.2	0.0	0.7	1.5	0.2	1.4
		2	5.4	0.3	0.1	0.2	0.0	0.5	0.0	0.0
		3	6.1	0.5	0.0	0.0	0.5	1.2	0.1	0.7
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-17-75 (1000 Miles)	1	1	6.7	0.0	0.5	0.0	0.0	1.2	0.0	0.0
		2	5.7	0.0	0.3	0.0	0.0	0.1	0.0	0.0
		3	6.6	0.0	0.5	0.0	0.0	1.0	0.0	0.0
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-17-75 (1000 Miles)	2	1	7.4	0.0	0.5	0.0	0.0	1.3	0.0	0.0
		2	6.1	0.0	0.1	0.0	0.0	0.2	0.0	0.0
		3	6.7	0.0	0.4	0.0	0.0	1.3	0.0	0.0
		BG	2.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-20-75 (2000 Miles)	1	1	6.5	0.0	0.5	0.0	0.0	0.8	0.0	0.0
		2	5.2	0.0	0.0	0.0	0.0	0.1	0.0	0.0
		3	6.2	0.0	0.5	0.0	0.5	1.3	0.0	0.9
		BG	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-20-75 (2000 Miles)	2	1	6.6	0.0	0.5	0.0	0.0	1.0	0.0	0.0
		2	5.6	0.0	0.2	0.0	0.0	0.0	0.0	0.0
		3	5.4	0.0	0.4	0.0	0.0	0.8	0.0	0.0
		BG	2.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0

APPENDIX C

INDIVIDUAL SULFUR AND NITROGEN COMPOUND DISTRIBUTION

TABLE C-1. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1972 CHEVROLET 350 CID ENGINE
(EM-214-F, Base Fuel at 0.1% S)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm		
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA
12-16-74 (0 miles)	1	1	ND	40	ND	--	ND	0.15	ND
		2	ND	ND	ND	--	ND	0.11	ND
		3	ND	ND	ND	--	ND	0.19	ND
		BG	ND	ND	ND	--	ND	ND	ND
12-16-74 (0 miles)	2	1	tr	tr	ND	--	ND	0.21	ND
		2	ND	ND	ND	--	ND	0.12	ND
		3	tr	tr	ND	--	ND	0.20	ND
		BG	ND	ND	ND	--	ND	ND	ND
12-23-74 (1000 miles)	1	1	ND	tr	ND	ND	ND	0.13	ND
		2	ND	tr	ND	ND	ND	0.05	ND
		3	ND	tr	ND	ND	ND	0.18	ND
		BG	ND	tr	ND	ND	ND	ND	ND
12-23-74 (1000 miles)	2	1	ND	tr	ND	ND	ND	0.16	ND
		2	ND	ND	ND	ND	ND	0.08	ND
		3	ND	tr	ND	ND	ND	0.14	ND
		BG	ND	ND	ND	ND	ND	ND	ND
12-31-74 (2000 miles)	1	1	ND	tr	ND	ND	ND	0.15	ND
		2	ND	tr	ND	ND	ND	0.06	ND
		3	ND	tr	ND	ND	ND	0.17	ND
		BG	ND	ND	ND	ND	ND	ND	ND
12-31-74 (2000 miles)	2	1	ND	tr	ND	ND	ND	0.16	ND
		2	ND	ND	ND	ND	ND	0.05	ND
		3	ND	ND	ND	ND	ND	0.16	ND
		BG	ND	ND	ND	ND	ND	ND	ND

*Hot start

ND - not detected

tr - trace

TABLEC-2. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1972 CHEVROLET 350 CID ENGINE
(EM-215-F, base fuel at 0.1% S + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm			
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA	
2-10-75 (0 miles)	1	1	ND	ND	ND	ND	ND	0.24	ND	
		2	ND	tr	ND	ND	ND	0.15	ND	
		3	ND	ND	ND	ND	ND	0.30	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
2-10-75 (0 miles)	2	1	ND	ND	ND	ND	ND	0.32	ND	
		2	ND	ND	ND	ND	ND	0.13	ND	
		3	tr	ND	ND	ND	ND	0.30	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
2-13-75 (1000 miles)	1	1	ND	ND	ND	ND	ND	0.31	ND	
		2	ND	tr	ND	ND	ND	0.15	ND	
		3	ND	ND	ND	ND	ND	0.32	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
2-13-75 (1000 miles)	2	1	ND	ND	ND	ND	ND	0.31	ND	
		2	ND	ND	ND	ND	ND	0.13	ND	
		3	ND	ND	ND	ND	ND	0.31	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
2-18-75 (2000 miles)	1	1	ND	tr	ND	ND	ND	0.18	ND	
		2	ND	ND	ND	ND	ND	0.13	ND	
		3	ND	ND	ND	ND	ND	0.31	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
2-18-75 (2000 miles)	1	1	ND	tr	ND	ND	ND	0.18	ND	
		2	ND	ND	ND	ND	ND	0.12	ND	
		3	ND	ND	ND	ND	ND	0.26	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	

*not start

ND = not detected

TABLE C-3. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1972 CHEVROLET 350 CID ENGINE
(EM-216-F, base fuel at 0.1%S + 0.486 g/gal Paradyne 506)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm		
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA
1-10-75 (0 miles)	1	1	ND	ND	ND	ND	ND	0.35	ND
		2	ND	ND	ND	ND	ND	0.14	ND
		3	ND	tr	ND	ND	ND	0.38	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-10-75 (0 miles)	2	1	ND	tr	ND	ND	ND	0.40	ND
		2	ND	ND	ND	ND	ND	0.21	ND
		3	ND	ND	ND	ND	ND	0.42	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-13-75 (1000 miles)	1	1	tr	tr	ND	ND	ND	0.18	ND
		2	tr	tr	ND	ND	ND	0.08	ND
		3	tr	tr	ND	ND	ND	0.20	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-13-75 (1000 miles)	2	1	ND	tr	ND	ND	ND	0.25	ND
		2	ND	ND	ND	ND	ND	0.14	ND
		3	ND	tr	ND	ND	ND	0.26	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-20-75 (2000 miles)	1	1	ND	ND	ND	ND	ND	0.41	ND
		2	ND	ND	ND	ND	ND	0.19	ND
		3	ND	ND	ND	ND	ND	0.55	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-20-75 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.48	ND
		2	ND	ND	ND	ND	ND	0.17	ND
		3	ND	ND	ND	ND	ND	0.50	ND
		BG	ND	ND	ND	ND	ND	ND	ND

*hot start

ND = not detected

tr = trace

TABLE C-4. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1972 CHEVROLET 350 CID ENGINE
(EM-231-F, base fuel at 0.1%S, 0.05 g/gal Pb + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm		
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA
3-11-75 (0 miles)	1	1	ND	ND	ND	ND	ND	0.26	ND
		2	ND	ND	ND	ND	ND	0.11	ND
		3	ND	ND	ND	ND	ND	0.26	ND
		BG	ND	ND	ND	ND	ND	ND	ND
3-11-75 (0 miles)	2	1	ND	ND	ND	ND	ND	0.26	ND
		2	ND	ND	ND	ND	ND	0.13	ND
		3	ND	ND	ND	ND	ND	0.25	ND
		BG	ND	ND	ND	ND	ND	ND	ND
3-14-75 (1000 miles)	1	1	ND	ND	ND	ND	ND	0.36	ND
		2	ND	ND	ND	ND	ND	0.14	ND
		3	ND	ND	ND	ND	ND	0.32	ND
		BG	ND	ND	ND	ND	ND	ND	ND
3-14-75 (1000 miles)	2	1	ND	ND	ND	ND	ND	0.40	ND
		2	ND	ND	ND	ND	ND	0.16	ND
		3	ND	ND	ND	ND	ND	0.23	ND
		BG	ND	ND	ND	ND	ND	ND	ND
3-21-75 (2000 miles)	1	1	ND	ND	ND	ND	ND	0.29	ND
		2	ND	ND	ND	ND	ND	0.13	ND
		3	ND	ND	ND	ND	ND	0.35	ND
		BG	ND	ND	ND	ND	ND	ND	ND
3-21-75 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.32	ND
		2	ND	ND	ND	ND	ND	0.13	ND
		3	ND	ND	ND	ND	ND	0.32	ND
		BG	ND	ND	ND	ND	ND	ND	ND

*hot start

ND = not detected

TABLE C-5. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1975 CHEVROLET 350 CID ENGINE
(EM-214-F, Base Fuel at 0.1% S)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm		
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA
12-17-74 (0 miles)	1	1	ND	ND	ND	--	ND	ND	ND
		2	ND	ND	ND	--	ND	ND	ND
		3	ND	ND	ND	--	ND	ND	ND
		BG	ND	ND	ND	--	ND	ND	ND
12-17-74 (0 miles)	2	1	ND	ND	ND	--	ND	0.05	ND
		2	tr	ND	ND	--	ND	tr	ND
		3	tr	tr	ND	--	ND	0.09	ND
		BG	ND	ND	ND	--	ND	ND	ND
12-20-74 (1000 miles)	1	1	ND	ND	ND	ND	ND	ND	ND
		2	ND	ND	ND	ND	ND	ND	ND
		3	ND	ND	ND	ND	ND	0.08	ND
		BG	ND	ND	ND	ND	ND	ND	ND
12-20-74 (1000 miles)	2	1	ND	ND	ND	ND	ND	0.08	ND
		2	ND	ND	ND	ND	ND	ND	ND
		3	ND	ND	ND	ND	ND	0.09	ND
		BG	ND	ND	ND	ND	ND	ND	ND
12-30-74 (2000 miles)	1	1	ND	ND	ND	ND	ND	0.11	ND
		2	ND	ND	ND	ND	ND	0.04	ND
		3	ND	ND	ND	ND	ND	0.11	ND
		BG	ND	ND	ND	ND	ND	ND	ND
12-30-74 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.12	ND
		2	ND	ND	ND	ND	ND	0.04	ND
		3	ND	ND	ND	ND	ND	0.14	ND
		BG	ND	ND	ND	ND	ND	ND	ND

*hot start

ND = not detected

tr = trace

TABLE C-6. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1975 CHEVROLET 350 CID ENGINE
(EM-215-F, base fuel at 0.1%S + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm			
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA	
2-7-75 (0 miles)	1	1	ND	ND	ND	ND	ND	0.11	ND	ND
		2	ND	ND	ND	ND	ND	0.06	ND	ND
		3	ND	ND	ND	ND	ND	0.13	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND
2-7-75 (0 miles)	2	1	ND	ND	ND	ND	ND	0.09	ND	ND
		2	ND	ND	ND	ND	ND	0.13	ND	ND
		3	ND	ND	ND	ND	ND	0.10	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND
2-14-75 (1000 miles)	1	1	ND	ND	ND	ND	ND	0.12	ND	ND
		2	ND	ND	ND	ND	ND	0.04	ND	ND
		3	ND	ND	ND	ND	ND	0.14	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND
2-14-75 (1000 miles)	2	1	ND	ND	ND	ND	ND	0.15	ND	ND
		2	ND	ND	ND	ND	ND	0.04	ND	ND
		3	ND	ND	ND	ND	ND	0.15	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND
2-17-75 (2000 miles)	1	1	ND	ND	ND	ND	ND	0.15	ND	ND
		2	ND	ND	ND	ND	ND	0.04	ND	ND
		3	ND	ND	ND	ND	ND	0.23	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND
2-17-75 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.30	ND	ND
		2	ND	ND	ND	ND	ND	0.06	ND	ND
		3	ND	ND	ND	ND	ND	0.32	ND	ND
		BG	ND	ND	ND	ND	ND	ND	ND	ND

*hot start

ND = not detected

TABLE C-7. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1975 CHEVROLET 350 CID ENGINE
(EM-216-F, base fuel at 0.1%S + 0.486 g/gal Paradyne 506)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm		
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA
1-9-75 (0 miles)	1	1	ND	199	ND	ND	ND	0.17	ND
		2	ND	tr	ND	ND	ND	0.06	ND
		3	ND	38	ND	ND	ND	0.20	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-9-75 (0 miles)	2	1	ND	tr	ND	ND	ND	0.12	ND
		2	ND	ND	ND	ND	ND	tr	ND
		3	ND	ND	ND	ND	ND	0.14	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-14-75 (1000 miles)	1	1	ND	ND	ND	ND	ND	0.20	ND
		2	ND	ND	ND	ND	ND	0.04	ND
		3	ND	ND	ND	ND	ND	0.25	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-14-75 (1000 miles)	2	1	ND	tr	ND	ND	ND	0.27	ND
		2	ND	ND	ND	ND	ND	0.08	ND
		3	ND	ND	ND	ND	ND	0.27	ND
		BG	ND	ND	ND	ND	ND	ND	ND
1-17-75 (2000 miles)	1	1	ND	tr	ND	ND	ND	0.11	ND
		2	ND	ND	ND	ND	ND	tr	ND
		3	ND	ND	ND	ND	ND	0.11	ND
		EG	ND	ND	ND	ND	ND	ND	ND
1-17-75 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.17	ND
		2	ND	ND	ND	ND	ND	0.16	ND
		3	ND	ND	ND	ND	ND	0.17	ND
		BG	ND	ND	ND	ND	ND	ND	ND

*hot start

ND = not detected

tr = trace

TABLE C-8. SULFUR AND NITROGEN COMPOUNDS DETERMINED
DURING 1975 LD FTP* WITH 1975 CHEVROLET 350 CID ENGINE
(EM-218-F, high aromatic fuel at 0.1%S + 0.378 g/gal Lubrizol 8101)

Date	Run	Bag	Sulfur Compounds, ppb				Nitrogen Compounds, ppm			
			H ₂ S	COS	CH ₃ SH	C ₂ H ₅ SH	NH ₃	CH ₃ NO ₂	DMNA	
3-10-75 (0 miles)	1	1	ND	tr	ND	ND	ND	0.11	ND	
		2	ND	ND	ND	ND	ND	tr	ND	
		3	ND	ND	ND	ND	ND	0.13	ND	
		BG	ND	tr	ND	ND	ND	tr	ND	
3-10-75 (0 miles)	2	1	ND	ND	ND	ND	ND	0.14	ND	
		2	ND	ND	ND	ND	ND	0.04	ND	
		3	ND	ND	ND	ND	ND	0.17	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
3-17-75 (1000 miles)	1	1	ND	ND	ND	ND	ND	0.15	ND	
		2	ND	ND	ND	ND	ND	0.04	ND	
		3	ND	ND	ND	ND	ND	0.18	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
3-17-75 (1000 miles)	2	1	ND	ND	ND	ND	ND	0.26	ND	
		2	ND	ND	ND	ND	ND	0.05	ND	
		3	ND	ND	ND	ND	ND	0.32	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
3-20-75 (2000 miles)	1	1	ND	ND	ND	ND	ND	0.16	ND	
		2	ND	ND	ND	ND	ND	0.03	ND	
		3	ND	ND	ND	ND	ND	0.20	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	
3-20-75 (2000 miles)	2	1	ND	ND	ND	ND	ND	0.18	ND	
		2	ND	ND	ND	ND	ND	0.03	ND	
		3	ND	ND	ND	ND	ND	0.21	ND	
		BG	ND	ND	ND	ND	ND	ND	ND	

*hot start

ND = not detected

APPENDIX D SULFUR DISTRIBUTION

TABLE D-1. SULFUR DISTRIBUTION* FOR 1972 350 CID CHEVROLET USING EM-214-F

Date	Miles	Run	Fuel S, g	S from SO ₂ , g		SO ₄ g	S from SO ₄ , g	% Fuel S Appearing as	
				bag	cont			SO ₂ (bag)	SO ₂ (cont)
12-16-74	0	1	2.64	4.79	7.17	2.39	3.59	90	136
12-16-74	0	2	2.59	5.30	6.88	2.65	3.44	102	133
		Avg.	2.62	5.05	7.03	2.52	3.52	96	135
12-23-74	1000	1	2.40	2.48	5.74	1.24	2.87	52	120
12-23-74	1000	2	2.25	3.01	5.80	1.51	2.90	67	129
		Avg.	2.33	2.75	5.77	1.38	2.89	60	125
12-31-74	2000	1	2.43	3.87	4.92	1.94	2.46	80	101
12-13-74	2000	2	2.35	3.77	5.61	1.89	2.80	80	119
		Avg.	2.39	3.82	5.27	1.92	2.63	80	110

* Based on hot start 1975 LD FTP

TABLE D-2. SULFUR DISTRIBUTION* FOR 1972 350 CID CHEVROLET USING EM-215-F

Date	Miles	Run	Fuel S, g	SO ₂ , g bag	SO ₂ , g cont	S from SO ₂ , g bag	SO ₄ , g cont	SO ₄ ⁼ g	S from SO ₄ ⁼ , g	% Fuel S appearing as SO ₂ (bag) SO ₂ (cont) SO ₄ ⁼	
2-10-75	0	1	2.56	4.81	7.04	2.41	3.52	0.0039	0.0013		138
		2	2.45	5.22	6.48	2.61	3.24	0.0045	0.0015		132
		3	2.47	5.23	6.55	2.62	3.28	0.0033	0.0011		133
		Avg.	2.49	5.09	6.69	2.55	3.35	0.0039	0.0013		134
											< 0.1
2-13-75	1000	1	2.40	5.15	6.59	2.58	3.30	0.0029	0.0010		138
		2	2.39	5.21	6.22	2.61	3.11	0.0016	0.0005		130
		Avg.	2.40	5.18	6.41	2.59	3.21	0.0023	0.0008		134
											< 0.1
2-18-75	2000	1	2.33	5.14	6.55	2.57	3.28	0.0028	0.0009		141
		2	2.35	4.81	6.19	2.41	3.10	0.0020	0.0007		132
		3	2.42	5.76	6.45	2.88	3.23	0.0026	0.0009		133
		Avg.	2.37	5.24	6.40	2.62	3.20	0.0025	0.0008		135
											< 0.1
											< 0.1
											< 0.1
											< 0.1

* Based on hot start 1975 LD FTP

TABLE D-3. SULFUR DISTRIBUTION* FOR 1972 350 CID CHEVROLET USING EM-216-F

Date	Miles	Run	Fuel		SO ₂ , g		S from SO ₂ , g		SO ₄ ⁼ g	S from SO ₄ ⁼ , g	% Fuel S appearing as		SO ₂ (cont)	SO ₄ ⁼
			S, g	bag	cont	bag	cont	SO ₂ (bag)			SO ₂ (cont)			
1/10/75	0	1	2.80	4.91	6.48	2.46	3.24	0.0034	0.0013	0.0013	88	116		< 0.1
		2	2.84	5.61	7.11	2.81	3.56	0.0028	0.0009	0.0009	99	125		< 0.1
		Avg.	2.82	5.26	6.80	2.64	3.40	0.0031	0.0011	0.0011	94	121		< 0.1
1/13/75	1000	1	2.53	4.42	6.08	2.21	3.04	0.0064	0.0021	0.0021	87	120		< 0.1
		2	2.35	4.76	5.47	2.38	2.74	0.0052	0.0017	0.0017	101	116		< 0.1
		Avg.	2.44	4.59	5.78	2.30	2.89	0.0058	0.0019	0.0019	94	118		< 0.1
1/20/75	2000	1	2.62	4.75	5.15	2.38	2.58	0.0071	0.0024	0.0024	91	98		< 0.1
		2	2.45	4.97	5.70	2.49	2.85	0.0068	0.0023	0.0023	102	116		< 0.1
		Avg.	2.54	4.86	5.43	2.44	2.72	0.0070	0.0024	0.0024	97	107		< 0.1

* Based on hot start 1975 LD FTP

TABLE D-4. SULFUR DISTRIBUTION* FOR 1972 350 CID CHEVROLET USING EM-231-F

Date	Miles	Run	Fuel S, g	SO ₂ , g		S from SO ₂ , g		SO ₄ ⁼ g	S from SO ₄ , g	% Fuel S appearing as		SO ₄ ⁼
				bag	cont	bag	cont			SO ₂ (bag)	SO ₂ (cont)	
3/11/75	0	1	2.54	4.20	6.71	2.10	3.36	0.0012	0.00004	83	132	< 0.1
		2	2.54	4.25	6.82	2.13	3.41	0.0010	0.0003	84	134	0.1
		Avg.	2.54	4.23	6.77	2.12	3.39	0.0011	0.00004	83	133	0.1
3/14/75	1000	1	2.45	4.93	6.99	2.47	3.50	0.0026	0.0010	101	143	0.1
		2	2.50	5.87	7.03	2.94	3.52	0.0018	0.0007	118	141	0.1
		3	2.43	5.76	6.88	2.88	3.44	0.0040	0.0013	119	142	0.1
		Avg.	2.46	5.52	6.97	2.76	3.49	0.0028	0.0009	112	142	0.1
3/21/75	2000	1	2.38	3.56	5.96	1.78	2.98	0.0021	0.0007	75	125	0.1
		2	2.42	3.89	6.26	1.95	3.13	0.0069	0.0023	81	129	0.1
		3	2.40	3.94	6.55	1.97	3.28	0.0012	0.0004	82	137	0.1
		Avg.	2.40	3.80	6.26	1.90	3.13	0.0034	0.0011	79	130	0.1

* Based on hot start 1975 LD FTP

TABLE D-5. SULFUR DISTRIBUTION* FOR 1975 350 CID CHEVROLET USING EM-214-F

Date	Miles	Run	Fuel S, g	SO ₂ , g		S from SO ₂ , g		SO ₄ ⁼ g	S from SO ₄ ⁼ , g	% Fuel S Appearing as SO ₂ (bag) SO ₂ (cont)		SO ₄ ⁼
				bag	cont	bag	cont					
12-17-74	0	1	2.28	2.36	3.57	1.18	1.79	0.169	0.056	52	79	2.5
12-17-74	0	2	2.17	2.56	3.04	1.28	1.52	0.178	0.059	59	70	2.7
		Avg.	2.23	2.46	3.31	1.23	1.66	0.174	0.058	56	75	2.6
12-20-74	1000	1	2.32	2.66	4.07	1.33	2.03	0.121	0.040	57	88	1.7
12-30-74	1000	2	2.27	3.26	4.18	1.63	2.09	0.106	0.035	72	92	1.5
		Avg.	2.30	2.96	4.13	1.48	2.06	0.114	0.038	65	90	1.6
12-30-74	2000	1	2.33	2.75	4.86	1.38	2.43	0.265	0.088	59	104	3.8
12-30-74	2000	2	2.34	2.83	3.76	1.41	1.88	0.237	0.079	60	80	3.4
		Avg.	2.34	2.79	4.31	1.40	2.16	0.251	0.084	60	92	3.6

* Based on hot start 1975 LD FTP

TABLE D-6. SULFUR DISTRIBUTION* FOR 1975 350 CID CHEVROLET USING EM-215-F

Date	Miles	Run	Fuel S, g	SO ₂ , g		S from SO ₂ , g		SO ₄ ⁼ g	S from SO ₄ ⁼ , g	% Fuel S appearing as SO ₂ (bag) SO ₂ (cont)		SO ₄ ⁼
				bag	cont	bag	cont					
2-7-75	0	1	2.36	4.73	4.80	2.37	2.40	0.23	0.076	101	102	3
		2	2.27	4.13	5.26	2.07	2.63	0.11	0.037	91	116	2
		3	2.29	4.73	5.98	2.37	2.99	0.19	0.063	103	131	3
		Avg.	2.31	4.53	5.35	2.27	2.67	0.18	0.058	98	116	3
2-14-75	1000	1	2.30	2.91	4.75	1.46	2.38	0.28	0.093	63	103	4
		2	2.22	3.19	4.80	1.60	2.40	0.29	0.097	72	108	4
		3	2.33	3.45	4.94	1.73	2.47	0.20	0.067	74	106	3
		Avg.	2.28	3.18	4.83	1.60	2.42	0.26	0.086	70	106	4
2-17-75	2000	1	2.30	3.43	4.93	1.72	2.47	0.375	0.125	75	107	5
		2	2.28	4.23	5.13	2.12	2.57	0.578	0.193	93	113	8
		3	2.33	4.51	5.29	2.26	2.65	0.392	0.131	97	114	6
		4	2.25	4.02	5.35	2.01	2.68	0.207	0.069	89	119	3
		Avg.	2.29	4.05	5.18	2.03	2.59	0.388	0.130	89	113	6

* Based on hot start 1975 LD FTP

TABLE D-7. SULFUR DISTRIBUTION * FOR 1975 350 CID CHEVROLET USING EM-216-F

Date	Miles	Run	Fuel S, g	SO ₂ , g		S from SO ₂ , g		SO ₄ = g	S from SO ₄ , g	% Fuel S appearing as SO ₂ (bag) SO ₂ (cont)		SO ₄
				bag	cont	bag	cont					
1/9/75	0	1	2.72	3.93	5.71	1.97	2.85	0.0547	0.0182	72	105	0.7
		2	2.34	3.05	5.28	1.53	2.64	0.1025	0.0342	65	113	1.5
		Avg.	2.53	3.49	5.50	1.75	2.75	0.0786	0.0262	69	109	1.1
1/14/75	1000	1	2.32	3.54	5.03	1.77	2.52	0.0927	0.0309	76	109	1.3
		2	2.34	4.06	5.15	2.03	2.58	0.1973	0.0658	87	110	2.8
		Avg.	2.33	3.80	5.09	1.90	2.55	0.1450	0.0484	82	110	2.1
1/17/75	2000	1	2.46	2.96	4.12	1.48	2.06	0.1531	0.0510	60	84	2.1
		2	2.40	2.73	4.47	1.37	2.24	0.2088	0.0696	57	93	2.9
		Avg.	2.43	2.85	4.30	1.43	2.15	0.1810	0.0603	59	89	2.5

* Based on hot start 1975 LD FTP

TABLE D-8. SULFUR DISTRIBUTION* FOR 1975 350 CID CHEVROLET USING EM-218-F

Date	Miles	Run	Fuel		SO ₂ , g		S from		SO ₄ = g	S from SO ₄ , g	% Fuel S appearing as		SO ₄ =
			S, g	bag	cont	bag	cont	SO ₂ , g			SO ₂ (bag)	SO ₂ (cont)	
3/10/75	0	1	2.44	4.15	4.53	2.08	2.27	0.332	0.110	85	93	5	
		2	2.34	4.25	4.97	2.13	2.49	0.466	0.154	91	106	7	
		3	2.35	3.21	4.30	1.61	2.15	0.378	0.125	69	91	5	
		Avg.	2.38	3.87	4.60	1.94	2.30	0.392	0.129	82	97	6	
3/17/75	1000	1	2.18	3.04	4.13	1.52	2.07	0.317	0.105	70	95	5	
		2	2.20	3.91	4.42	1.96	2.21	0.489	0.161	89	100	7	
		3	2.21	3.72	4.60	1.86	2.30	0.386	0.127	84	96	6	
		Avg.	2.20	3.56	4.38	1.78	2.19	0.397	0.131	81	97	6	
3/20/75	2000	1	2.26	1.64	3.11	0.82	1.56	0.460	0.152	36	69	7	
		2	2.19	2.77	3.37	1.39	1.69	0.564	0.186	63	77	8	
		3	2.21	3.12	3.85	1.93	1.92	0.584	0.193	87	87	9	
		Avg.	2.22	2.51	3.44	1.38	1.72	0.536	0.177	62	78	8	

* Based on hot start 1975 LD FTP